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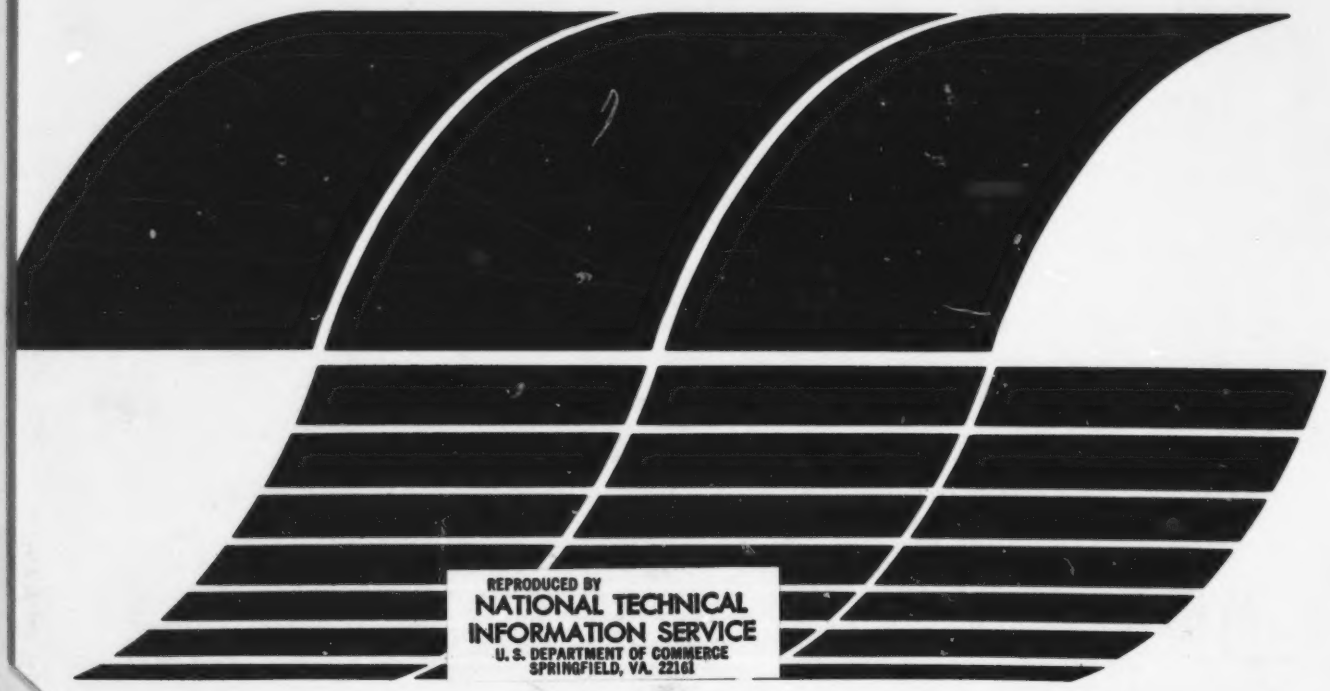

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EPA-600/7-79-243
November 1979

CHARACTERIZATION OF VISIBILITY-REDUCING AEROSOLS IN THE SOUTHWEST

Project VISTTA Progress Report No. 1

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ABSTRACT

The atmospheric visibility-reducing aerosol in the Southwest has been experimentally characterized in the Fall, 1977, with respect to particle size, composition, and contribution to light scattering. Measurements were taken within the mixing layer using the MRI instrumented Beechcraft Queen Air aircraft. The aircraft was equipped to measure and record on magnetic tape the light-scattering coefficient, Aitken nuclei count, size distribution, ozone, sulfur dioxide, nitrogen oxides, temperature, dew point, turbulence, pressure (altitude), and navigational parameters. Multistage impactor and size-fractionated filter samples were also collected in order to determine aerosol elemental composition as a function of size. Visual range estimates were obtained by viewing distant landmarks and verified by optical photography.

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SECTION 1

INTRODUCTION

BACKGROUND

The southwestern United States desert and mountain areas, shown in Figure 1, are generally characterized by very good visibility (~100 km). Until recent years, scenic vistas of natural landmarks and mountains with a visual range of over 100 miles were common. These vistas have been considered a major resource of the Southwest, and numerous national parks, forests, and monuments have been created to preserve them. The tourism resulting from the southwest scenery has played a major role in the economy of the region.

As the population of the region has grown, there has been an apparent reduction in the average visibility (Trijonis and Yuan, 1978). Residents of the Southwest are concerned about this loss and point to various anthropogenic activities as the cause. This concern has led to the August, 1977, amendments to the Clean Air Act, which contain a section stating, "as a national goal the prevention of any future, and the remedying of any existing, impairment of visibility in mandatory Class I Federal areas which impairment results from man-made air pollution." Previously, however, comprehensive studies had not been performed to quantify and determine the cause of the current problem or to provide the basis for a control strategy to keep the problem from getting worse.

Visibility impairment in the atmosphere is due primarily to the presence of small particles which scatter and absorb light and, secondarily, to NO_2 which absorbs blue light (Charlson, Waggoner, and Thielke, 1978). In the southwest, a regional decrease in visibility is likely due to the long-range transport of aerosol or gaseous precursors into unpopulated pristine areas. A second possible cause of regional visibility impairment may be wind-blown dust. Both types of particle may be of anthropogenic origin. Some of the varied activities which may contribute to the decline in visibility are: increased population and the resulting increase in automotive emissions; emissions from power plants; emissions from smelters; disturbance of the topsoil and desert pavement due to agriculture, grazing, and off-road vehicles; and mining activities.

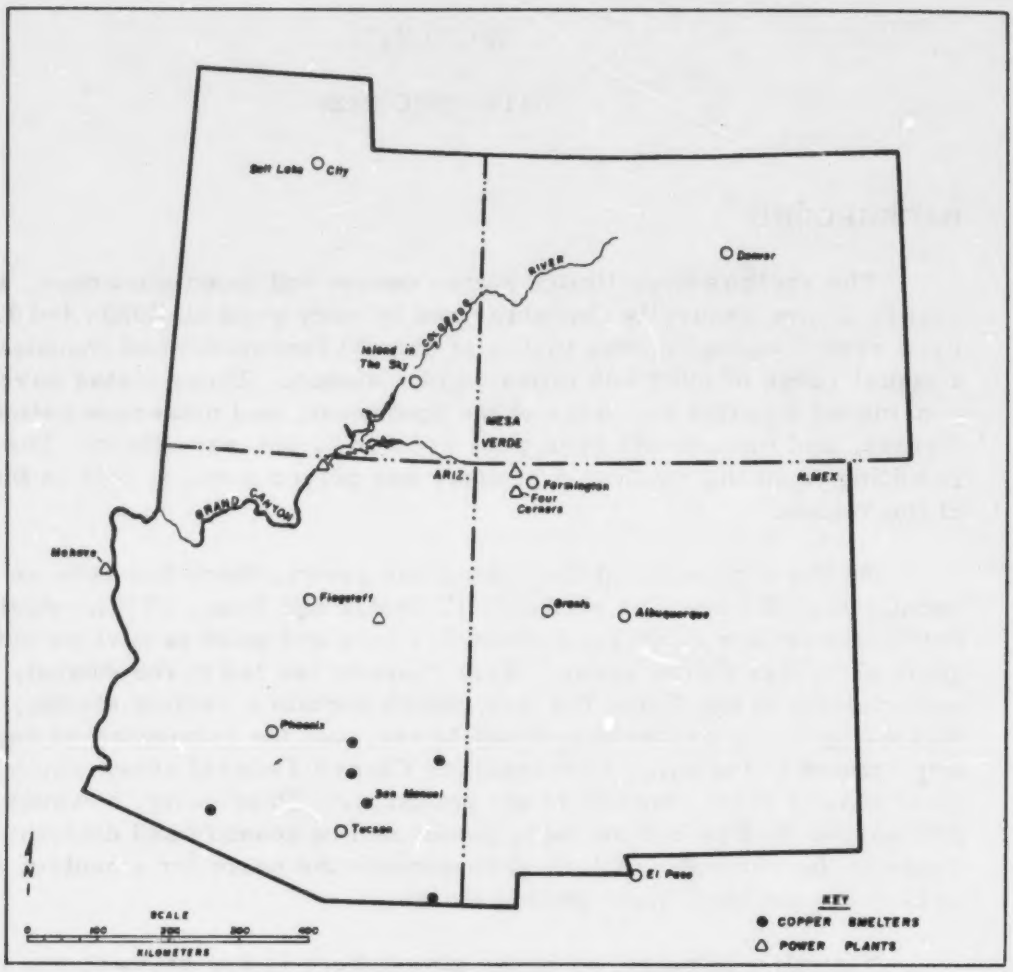

Figure 1. Map of Southwestern United States.

In addition to their scenic value, the mountain and desert regions of the Southwest represent a major energy resource. Coal, oil, natural gas, oil shale, uranium, and abundant sunlight are all found in the area. The emerging national priority of developing domestic energy supplies will accelerate the development of the Southwest's energy resources. If not planned properly, this development could lead to greater visibility impairment and loss of scenic resources.

Project VISTTA,* sponsored by the EPA Environmental Science Research Laboratory in Research Triangle Park, North Carolina, has been initiated to determine the sources of visibility reduction in the Southwest and to help resolve the potential conflict between the congressional mandate for improved visibility and the need for increased energy production.

The experimental approach of Project VISTTA is to characterize the visibility-reducing species in the atmosphere, namely particulate matter and NO_2. To determine the relative contribution of the various anthropogenic activities to visibility degradation, and thus to develop control strategies, the VISTTA project has concentrated on the study of the size distribution and chemistry of the visibility-reducing aerosol in the region. This defines the problem. At the same time, data have been collected to characterize the emissions from some of the activities mentioned above, i.e., their size distribution and chemistry, and the transport and transformations these emissions undergo in the atmosphere. Knowing both the characteristics of the atmospheric aerosol and of the emissions, the relative contribution of each type of emission to the overall problem can be determined (Friedlander, 1977).

It has been estimated (Trijonis and Yuan, 1978) that in the southwest region between 30 and 60 percent of the light extinction due to particles is caused by sulfates. One of the sources of sulfur compounds in the atmosphere is the burning of sulfur-containing fuel for power generation. As part of Project VISTTA, the EPA would like to quantify the contribution of the power industry to visibility impairment in the Southwest.

OBJECTIVES

The objectives of Project VISTTA are as follows:

---

* VISTTA is an acronym from Visibility Impairment due to Sulfur Transport and Transformation in the Atmosphere

1. To characterize the visibility-reducing aerosol in the Southwest with respect to particle size, chemical composition as a function of size, and spatial distribution. To meet this goal, measurements will be taken on a regional scale (flight paths up to 1000 km) and at points near urban centers, power plants and smelters in the region.

2. To characterize the emissions which are important in visibility reduction from typical power plants and smelters in the region. Both primary particulate emissions and gaseous aerosol precursors will be taken into account.

3. To determine the detailed contributions to light scattering for the Southwest region broken down by chemical composition and size (light scattering budget).

4. To quantitatively assess the contributions of various sources, both anthropogenic and natural, to the visibility-reducing aerosol. Of particular interest is the contribution of emissions from power plants.

The first experimental portion of Project VISTTA was aimed at the first three objectives. This first study was a preliminary experiment, and the data are rather limited. These results are summarized in Section 5 of this report. In the later stages of the project, the fourth objective will be more fully addressed. An outline of the future direction of the project is given in Section 3 of this report.

RESPONSIBILITIES

Project VISTTA is a team project involving several groups. The groups involved in the initial sampling period (October 1 - 10, 1977) and subsequent analysis and their responsibilities are as follows:

Meteorology Research, Inc. (MRI) -- Project planning, design, and coordination, aircraft sampling, and data analysis.

EPA - Environmental Science Research Lab (ESRL) at Research Triangle Park -- Calibration of aircraft instruments.

University of California - Davis (UCD) -- Elemental Analysis of samples from a specially designed UCD airborne impactor.

University of Washington (UW) -- Ground-based measurements of size distribution, light scattering, and light absorption coefficients.

California Institute of Technology (CIT) -- Data analysis.

The individuals involved in the MRI portion of the program, their affiliations, and responsibilities are given below:

Project Coordinator	D. L. Blumenthal (MRI)
Senior Data Analyst	E. S. Macias (CIT, Consultant to MRI on leave from Washington University, St. Louis)
Field Manager	J. A. Anderson (MRI)
Data Analysis	B. K. Cantrell (SRI International)
Data Analysis	S. K. Friedlander (UCLA)
Data Analysis	J. A. Ogren (MRI and UW)
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EPA Project Officer	W. E. Wilson (EPA) T. Ellestad (EPA)

SECTION 2

SUMMARY AND CONCLUSIONS

The atmospheric visibility-reducing aerosol in the Southwest has been experimentally characterized with respect to particle size, composition, and contribution to light scattering. Measurements were taken within the mixing layer using the MRI instrumented Beechcraft Queen Air aircraft. The aircraft was equipped to measure and record on magnetic tape the light-scattering coefficient, Aitken nuclei count, size distribution, ozone, sulfur dioxide, nitrogen oxides, temperature, dew point, turbulence, pressure (altitude), and navigational parameters. Multistage impactor and size-fractionated filter samples were also collected in order to determine aerosol elemental composition as a function of size. Visual range estimates were obtained by viewing distant landmarks and verified by optical photography.

The multistage impactor was mounted in the nose of the aircraft. The impactor stages had 50 percent collection efficiency for aerosol aerodynamic diameters of 4, 2, 1 and 0.5 microns. Impactor samples were collected on greased Mylar film. A Nuclepore final filter was used to collect all particles not collected on the four impaction stages. The impactor samples were analyzed by particle-induced X-ray emission. The fine particle samples from a TWOMASS two-stage filter sampler were analyzed by flash vaporization - flame photometric detection.

The 1977 field program consisted of seven sampling days. The experimental data included flights of the region on three full days and parts of one other, flights in the plume of a copper smelter (San Manuel smelter) on three days, and flights in the plume of a coal-fired power plant (Mohave power plant) on one day.

The regional flights were designed to characterize the visibility-reducing aerosol within 500 m of the surface on flight paths over 250 km. On two days, the total flight paths were over 1000 km. The visibility along these paths was documented with a high-sensitivity nephelometer, a camera, and visual range measurements from aircraft to prominent landmarks.

A description of the 1978 field program and recommendations for future studies are given.

This study is the first of several similar studies. It should be considered as a pilot study and all results should be considered preliminary and limited. The results of the Fall, 1977, study are summarized below:

1. On two regional flights over large parts of the Southwest, the visibility-reducing aerosol was quite homogeneous throughout the entire region, indicating that the visibility impairment was of regional extent.

2. The aerosol size distribution throughout the region on October 5 and 9, 1977, was bimodal, with a geometric volume mean size for the fine particles of ~ 0.25 microns, which is slightly smaller than the continental background aerosol average mean size (0.3 microns). The measured coarse particle mode volumetric mean size was ~ 5.5 microns, which is equal, within error, to the continental background.

3. The elemental size distribution from both regional and plume impactor samples indicated that aluminum, calcium, and iron are present predominantly in coarse particles; sulfur and titanium are present predominantly in fine particles; and silicon and potassium have substantial concentrations in both modes.

4. Sulfur and silicon were found in nearly equal concentrations in the Southwest background data and were the elements present in the highest contrations in the fine particles ($D_p \leq 1\mu m$). The detailed aerosol mass balance determined for the Southwest region showed that sulfur (expressed as ammonium sulfate) and silicon (expressed as SiO_2) amounted to ~ 50 percent and ~ 30 percent of the fine particle mass, respectively.

5. On the days sampled, a total of ~ 90 percent of the measured coarse particle ($D > 1\mu m$) mass in the Southwest region was composed of elements which were present in the same abundance relative to aluminum as in the earth's crust. This indicates that the source of these particles is either wind-blown dust or material with an elemental composition nearly that of crustal material, such as flyash.

6. The light-scattering budget for Southwest background aerosol on October 9, 1977, indicated that ~ 50 percent of the light scattering was due to fine particles, ~ 40 percent was due to Rayleigh scattering from gases, and ~ 4 was due to coarse particles. Considering only the light scattering due to particles, ~ 90 percent is due to fine particles which are composed mainly of sulfates [~ 50 percent as $(NH_4)_2 SO_4$)] and silicon compounds ~ 30 percent as SiO_2).

7. Mie scattering calculations of the light scattering coefficient due to particles using the measured average regional size distribution were

in good agreement with the values measured with a nephelometer. This is a quantitative indication of the internal consistency of the size distribution and b_{scat} measurements which adds credibility to the calculated light-scattering budget.

8. Plume excess fine particle aerosol, i.e., the point source emission plume aerosol with the background subtracted, was composed largely of sulfur and silicon compounds for both the smelter and power plant plumes. The major elemental species in the plume excess coarse particle aerosol were aluminum, silicon, potassium, calcium, and iron in approximately crustal abundances in both plumes. These results indicate that fine particle Si may be a good tracer for primary combustion aerosol in smelter and power plant plumes.

9. A simple semi-quantitative calculation of visual plume impact is described which compares the visual range with and without the plume present. On October 4, 1977, the smelter plume caused an ~ 90 percent reduction of visual range relative to the background visual range (135 km) at 8 km downwind from the plant. As far as 127 km downwind, increased b_{scat} and sulfate levels relative to background concentrations were observed along with an ~ 40 percent reduction of visual range due to the smelter plume.

10. Sulfate aerosol was formed in Southwest power plant and smelter plumes. The measured SO_2 conversion rate from the San Manuel copper smelter on one morning between 0900 and 1230 (MST) was 0.7±0.2 percent/hour between 60 and 127 km downwind.

11. The plume excess visibility budget indicated that fine particle sulfur and silicon species contribute ~ 50 percent to the excess b_{scat} in the San Manuel smelter plume. In the Mohave power plant plume coarse particles were the major contributors to the excess b_{scat}, which may have been at least partially due to measurement interferences from wind-blown dust on the sampling day.

SECTION 3

FUTURE PLANS AND RECOMMENDATIONS

RECOMMENDATIONS FOR FUTURE EXPERIMENTS

The initial exploratory experiments of Project VISTTA were productive. The characterization of the visibility-reducing aerosol with respect to chemical composition(particle size, and spatial distribution in remote areas and near sources was successful. However, these results indicate a number of improvements and changes needed in future experiments in order to meet the VISTTA goals described in the Introduction of this report.

The recommended improvements and changes are described below. Some have been incorporated into the September 1978 VISTTA experiments as described later in this section. In addition, Systems Applications, Inc., has suggested a number of measurements (SAI, 1978) to validate their visibility models (Latimer et al., 1978). Many of these measurements are already part of the VISTTA experimental plan. Those additional measurements which are compatible with the goals and measurements of the VISTTA program are also included in the following discussion:

1. Total aerosol mass data for at least two size ranges are needed. This is essential for both source identification and aerosol characterization. Aerosol mass can be determined by gravimetric weighing, beta absorption, or use of a piezoelectric crystal.

2. An improved impactor is needed to extend the size separation of particles down to approximately 0.1 μm in diameter. This increased size resolution is needed for a more accurate determination of the visibility budget, that is, the contributions of the various chemical species to light scattering. The impactor used in the initial studies has a 50 percent efficiency cutoff for the final stage of 0.5 μm aerodynamic diameter which is near the peak of the curve of scattering efficiency per unit mass versus particle size (Figure 8). Furthermore, the volume distribution in the Southwest, as described in Section 3, peaks in the range of 0.1 to 0.3 μm. Thus, data on chemical composition as a function of size are most important in the size range from 0.1 to 1.0 μm. An eight-stage, low-pressure

impactor with 50 percent efficiency cutoffs of 4.0-, 2.0-, 1.0-, 0.5-, 0.26-, 0.11-, 0.076-, and 0.05-μm aerodynamic diameter which would be suitable for aerosol collection in VISTTA has been developed by Hering, Flagan, and Friedlander at CIT (Hering et al., 1978). This instrument was tested in the MRI aircraft and on the ground in the September 1978 VISTTA field program. Particles are impacted on stainless steel strips for sulfate and nitrate analysis in the present configuration, but it could be modified to accommodate Mylar impaction surfaces needed for PIXE analysis.

3. Improved data on the concentration of the major chemical constituents -- sulfate, nitrate, silicon, and carbon -- are needed for aerosol characterization. Wherever possible, more than one technique should be used to determine the concentration of each element in order to validate results. In the 1977 experiments, particulate sulfur was measured by both PIXE and FV-FPD, but there were no redundant measurements of other elements.

   In future experiments, particulate nitrate in at least two size ranges should be measured. Several methods are available which are sensitive enough for use with relatively short aircraft sampling times, such as ion chromatography (IC) (Mulik et al., 1976) or flash vaporization and gas phase chemiluminescence detection with an NO_x monitor (Hering, 1978). The IC analysis will also give sulfate concentration which can be used as a determination of the chemical composition of the total aerosol sulfur as determined by PIXE analysis of impactor samples.

   Silicon was found to be a major constituent of fine particles in remote areas in the 1977 VISTTA experiments using PIXE analysis of impactor samples. In some cases, the silicon concentration exceeded the sulfur concentration. However, the low energy of silicon x-rays results in poor sensitivity. It is therefore necessary to measure silicon by another, more sensitive technique to verify these results. A sensitive method is flameless atomic absorption (AA), but we have found no reference to its use for this purpose. A less sensitive alternative is conventional flame AA (Moyers et al., 1977).

   Measurements of total carbon, soot carbon, and aerosol absorption are needed for a complete characterization of the aerosol and for completing the Southwestern visibility budget. Carbon is a major constituent of fine particles near urban areas, with as much as 50 percent of the carbon in the form of soot (Macias et al., 1978b). In this form, this constituent is the major contributor to particle absorption of light and, therefore, is important to visibility reduction in urban areas Rosen et al., 1978). Diesel motor vehicles are a major source of fine particle soot carbon (Pierson, 1978); coal combustion in a modern power plant is thought to be a relatively minor source (Nolan, 1978).

Measurements of particle absorption in the Southwest indicate that the ratio of particle absorption to total extinction is 10 percent in clean background areas in the Southwest and up to 50 percent in urban areas (Weiss et al., 1978). Total carbon can be measured by inelastic proton scattering followed by gamma ray analysis of light elements (GRALE) (Macias et al., 1978b) or aerosol combustion with detection of the evolved carbon dioxide or methane (Grosjean, 1975; Huntzicker and Johnson, 1978; and Macias, 1978a). Soot carbon can be measured by the GRALE technique after the volatile organic carbon compounds have been removed by heating. An alternate method for estimating fine particle carbon measures the reflectance from a white glass filter (Macias et al., 1978b). Aerosol absorption can be measured by the Integrating Plate Method, a technique based on the transparency of a thin filter containing a small amount of aerosol (Lin et al., 1973).

4. More sensitive and extensive data of trace elements are needed for source characterization studies. PIXE analysis for elements such as silicon, sulfur, iron, etc. should be combined with neutron activation analysis for elements such as selenium, arsenic, antimony, etc., seen in earlier studies (Ragaini and Ondov, 1977). Some of these elements can be detected by both methods, which will act as a check on the analysis technique.

5. Sampling should be carried out when the scattering due to particles is greater than 40×10^{-6} m^{-1} in large parts of the region. Observations from aircraft indicate that occasionally areas of reduced visibility ~100 km across exist in pristine areas of the Southwest surrounded by areas of very good visibility (Beil, 1978). However, it has been estimated by visual range observations that in pristine areas of the Southwest these low visibility conditions exist only ~15 percent of the time (Latimer et al., 1978). Aircraft sampling under these conditions would lead to an estimate of the spatial distribution of the visibility-reducing aerosol. In addition, this would result in much more detailed elemental data and would greatly facilitate source characterization studies.

6. Sampling should be carried out at different times of the year, particularly at times when the visibility impairment in the Southwest is predicted to be greatest. Examination of seasonal visibility patterns (Roberts et al., 1975) shows that the lowest values of visual range in the Southwest are observed in the summer months. It has been suggested that, in the Southwest, stable conditions occur most frequently in the winter, which should result in the greatest plume visibility impairment (SAI, 1978). However, background visual range is greatest during the winter.

FALL 1978 EXPERIMENTAL DESIGN

The second set of field experiments in Project VISTTA was carried out September 12-27, 1978. The instrumented MRI Beechcraft Queen Air aircraft was again used for airborne sampling. This was augmented by an expanded ground-based measurement program. The field measurements were based in Farmington, New Mexico, during the first 10 days of the program. Flights in the plume of the Four Corners Power Plant were carried out during six days; regional sampling was performed on two days. The last six days of the program were based in Tucson, Arizona, where the aircraft was flown in smelter and urban plumes and on flights throughout the region.

The instrumentation used in the 1977 experiments was flown in the aircraft (Table 1). However, a number of improvements, recommended earlier in Section 4, were made in this second experimental period. A Washington University St. Louis aerosol charger (Husar, Macias, and Dannevick, 1976) was added to the instrumentation package. This instrument gives an on-line measurement which is most sensitive to particles in the size range of 0.01- to 0.2- μm diameter (Sverdrup, 1977). A cyclone separator with backup filters was operated on most 1978 flights. One filter was Teflon-coated glass used for ion chromatography analysis of sulfate and nitrate. Occasionally a second backup Nuclepore filter was used for determining aerosol absorption by the Integrating Plate Method. A Caltech low-pressure impactor was installed on some of the flights in place of the Nuclepore filter to determine the detailed sulfur size distribution. The impactor stages were analyzed for sulfur using flash vaporization followed by gas phase flame photometric detection (Roberts and Friedlander, 1976). Fine particle aerosol mass was determined gravimetrically from the filters. The final filter from some of the UCD impactor samples will be analyzed for trace elements by neutron activation analysis. A few of the TWOMASS sampler fine particle filter samples will be analyzed for carbon, sulfur, and nitrogen before FV - FPD sulfur analysis.

Ground-based measurements were greatly expanded in the 1978 experiments. The measurements carried out in the Four Corners area and at Mesa Verde National Park are outlined in Table 2. With this more comprehensive set of aircraft and ground-based measurements, it is expected that a more detailed characterization of the visibility-reducing aerosol will be possible.

TABLE 1. BEECHCRAFT QUEEN AIR INSTRUMENTATION

Measured Parameter	Instrument
Aerosols - Integral Size:	
Light Scattering	MRI 1562 Nephelometer (modified by UW for high sensitivity)
Aitken Nuclei	Environment One Condensation Nuclei Monitor
Aerosols - Differential Size:	
Particle Diameter -	
0.01 – 1.0 μm	TSI 3030 Electrical Aerosol Size Analyzer (EAA)
0.5 - 4.0 μm	Royco 218 Optical Particle Counter (OPC)
2.0 - 30.0 μm	Particle Measurement Systems Axial Scattering Probe (ASP)
Aerosol Samples:	
Two Stage Sampler	MRI TWOMASS Sampler
Multistage Impactor	UCD Impactor System
Gases:	
Ozone	REM 612 O_3
Sulfur Dioxide	Meloy 285 Total Sulfur Monitor
Nitrogen Oxides	Monitor Labs 8440 NO - NO_x
Other:	
Dew Point, Temperature, Turbulence, Altitude, Indicated Air Speed	Cambridge Systems 137 / MRI Airborne Instrument Package
Position - VOR, DME	Aircraft Navigation System
Visual Range	Optical Photography

TABLE 2. GROUND-BASED MEASUREMENTS, 1978 EXPERIMENTS

Parameter	Sampling Device/ Analysis Technique	Analysis Responsibility
Four Corners Area:		
Size Distribution	EAA, OPC	CIT
Light Scattering	Nephelometer	CIT
Sulfate Size Distribution	LPI - FV/FPD	CIT
Nitrate Size Distribution	LPI - FV/ Chemiluminescence	CIT
Mass[1], Sulfate[2], Nitrate[2]	Cyclone Separator with Teflon Filter [1]Gravimetric Weighing [2]Ion Chromatography	CIT ERT
Carbon	TWOMASS Sampler/GRALE	WU
NH_3	Tandem Filter	Rockwell Internat'l
Plume Optics	Telephotometer	EPA - LV New Mexico Health
Wind Speed Wind Direction	Pibal	MRI
Mesa Verde National Park:		
Size Distribution	EAA, OPC	UW
Light Scattering	Nephelometer	UW
Aerosol Absorption	IPM	UW
Silicon	AA	Univ. of Arizona

SECTION 4

PROGRAM DESCRIPTION

The initial exploratory field program of Project VISTTA was carried out October 1 - 10, 1977. This initial phase was designed to outline the extent and nature of the visibility impairment in the Southwest. The emphasis was placed on obtaining as complete a characterization of the aerosol as possible in order to aid in planning a more optimal set of experiments in the later stages of the VISTTA program.

Measurements were taken within the mixing layer (< 500 m above ground level) using the instrumented MRI Beechcraft Queen Air aircraft. This twin-engine aircraft has minimum and maximum sampling speeds of 180 and 290 km/hr, respectively. With a full instrument complement, the maximum sampling time is over four hours. The aircraft was equipped to to continuously measure and record on magnetic tape light-scattering coefficient, Aitken nuclei count, ozone, sulfur dioxide, nitrogen oxides, temperature, dew point, turbulence, pressure (altitude), and navigational parameters. Aerosol size distribution measurements were made over a range of 0.01 to 30 μm using three size-selective aerosol sensors. An electrical aerosol analyzer and optical particle counter were used in conjunction with an automated "grab bag" sampling system designed to collect and hold a discrete static air sample for analysis (Blumenthal et al., 1978). An axial scattering probe was operated in the free stream near the nose of the aircraft for particle size measurements in the range of 2 to 30 μm. Multistage impactor and two-stage filter sampler samples were also collected in order to determine the elemental composition as a function of size. The details of the aircraft instrumentation are given in Table 1. Visual range measurements were carried out by viewing distant landmarks and verified by optical photography.

Gas instrument calibration was carried out by personnel from the EPA - ESRL. The nephelometer was calibrated with Freon-12 (b_{scat} = 235 x 10^{-6} m^{-1} at 525 nm, sea level) and filter air (b_{scat} = 15 x 10^{-6} m^{-1} at 525 nm, sea level). A gas phase titration was used to calibrate the O_3 and NO monitors. The SO_2 monitor was calibrated with a permeation tube.

The multistage impactor, a Lundgren-type impactor specially modified for aircraft sampling by investigators at University of California at Davis (UCD), was mounted in the nose assembly of the aircraft. The impactor stages had 50 percent collection efficiency for particle diameters of 4, 2, 1, and 0.5μm. Impactor samples were collected on greased Mylar film. A Nuclepore final filter was used to collect all particles not collected on the four impaction stages. The impactor samples were analyzed by particle-induced X-ray emission (PIXE) (Cahill, 1975) at the Crocker Nuclear Lab cyclotron at UCD. This analysis gives elemental concentration of elements with atomic numbers of 13 (Al) or greater.

The fine particle samples from the TWOMASS two-stage sampler (Macias and Husar, 1976) were analyzed by flash vaporization-flame photometric detection (Husar et al., 1975) by J. D. Husar and Associates (St. Louis, MO).

The field program, summarized in Table 3, consisted of seven sampling days. The experimental plan included flights of the region on three full days and parts of one other, flights in the plume of a copper smelter (San Manuel smelter) on three days, and flights in the plume of a coal-fired power plant (Mohave power plant) on one day.

The regional flights were designed to characterize the visibility-reducing aerosol on flight paths of over 300 km. On two days the total flight paths were over 1000 km. All flights were within the mixing layer; however, occasional spirals were made to define the mixing layer structure. The visibility along these paths was documented with a high-sensitivity nephelometer, a camera, and with visual range measurements from the aircraft to prominent landmarks. Ground measurements were made by UW at Canyonlands National Park with a nephelometer and sampler for aerosol absorption.

Smelter plume flights were carried out at several downwind distances up to 127 km from the San Manuel smelter. Flights in the 1580 MW Mohave power plant plume were performed at distances as far as 62 km downwind of the plant.

The plume flight patterns were designed to provide a detailed characterization of the plume at discrete distances downwind from the source. At each distance horizontal traverses were made through the plume normal to the plume axis at several elevations. Traverses were long enough to include background air on either side of the plume. Vertical spirals were also performed to help characterize the plume structure. In addition to cross-sectional plume traverses, orbital flights within the plume of up to

TABLE 3. VISTTA FIELD PROGRAM SUMMARY - 1977

Date	Flight Description	Flight Times (MDT) Start	Stop	Flight Hours	Plume Sampling Distance (km)	Comments
10/ 1/77	San Manuel and Hayden Smelters (AZ)	6:17	9:30	3.2	3, 14	Plume Weak and Scattered
10/ 2/77	San Manuel Smelter	9:42	14:15	4.6	8, 32, 60	Plume Definition Fair
10/ 4/77	San Manuel Smelter	8:35	12:45	4.2	60, 127	Plume Well Defined
	Phoenix Urban Plume	13:35	16:15	2.7		
10/ 5/77	Flagstaff (AZ) - Island in the Sky (UT) -	10:11	13:32	3.3		Regional Sampling
	Farmington (NM) - Grants (NM) - Flagstaff	14:45	17:30	2.7		
10/ 8/77	Mohave Power Plant (NM)	10:02	14:43	4.7	32, 62	Plume Diluted, due to Intense Mixing
		16:05	16:44	0.7		
	Mohave - Flagstaff	16:44	17:44	1.0		Regional Sampling
10/ 9/77	Flagstaff - Grants - Farmington -	10:04	12:36	2.5		Regional Sampling
	Island in the Sky - Flagstaff	14:03	17:56	3.9		
10/10/77	Flagstaff - Needles (CA) - Upland (CA)	6:39	11:00	4.4		Regional Sampling

one hour were carried out at each distance to gather heavily loaded impactor and filter samples. Orbits upwind of the source were flown to gather background samples.

Single theodolite pilot balloon (pibal) releases were carried out at various times on every sampling day to determine wind direction and speed as a function of altitude in the sampling area.

SECTION 5

SUMMARY OF RESULTS FROM FALL 1977 EXPERIMENTS

CHARACTERIZATION OF THE VISIBILITY-REDUCING AEROSOL IN THE SOUTHWEST

Spatial Distribution

The character of visibility-reducing aerosols in the Southwest was determined in long regional flights in order to measure a regional background. These flights were made between or upwind of large point sources of pollutants, such as urban areas and power plants. All flights were at a constant altitude to within ±25 m. On October 5, 1977, flights were made between Flagstaff (AZ) - Tuba City (AZ) Island in the Sky - Farmington (NM) - Grants (NM) Flagstaff, as shown in Figure 2. The flights on October 9 followed the same 1080-km path in the reverse direction. Shorter flights in the region (~260 km) were flown on October 8 and 10. On all days, the visibility and air quality were quite good (average visual range = 140 km). This resulted in very low values for all measured aerosol and gas parameters except ozone, which was present in concentrations representative of clean air. Therefore, only data from the longer flights on October 5 and 9 which have more meaningful averages, given in Table 4, are discussed in this report. The averages for each day were determined by averaging over each segment of the flight and then averaging the flight segment averages. The NO, NO_x, and SO_2 concentrations were below the sensitivity of the monitors throughout the region. The b_{scat} values, although quite low, were detectable with the aircraft instrumentation. The light scattering coefficient values b_{scat}, given in Table 3, are from the nephelometer output with the contribution of Rayleigh scattering of air molecules included.

TABLE 4. AVERAGE PARAMETERS MEASURED DURING REGIONAL FLIGHTS

Date	Altitude (MSL)	Flight Length (km)	b_{scat} ($\times 10^{-6} m^{-1}$)	SO_2 (ppb)	O_3 (ppb)	NO (ppb)	NO_2 (ppb)
10/5/77	2428±23	1080	28±3[a]	<1	33±4	<5	<5
10/9/77	2289±21	1080	25±1	<1	38±5	<5	<5

[a] All ± values are standard deviations.

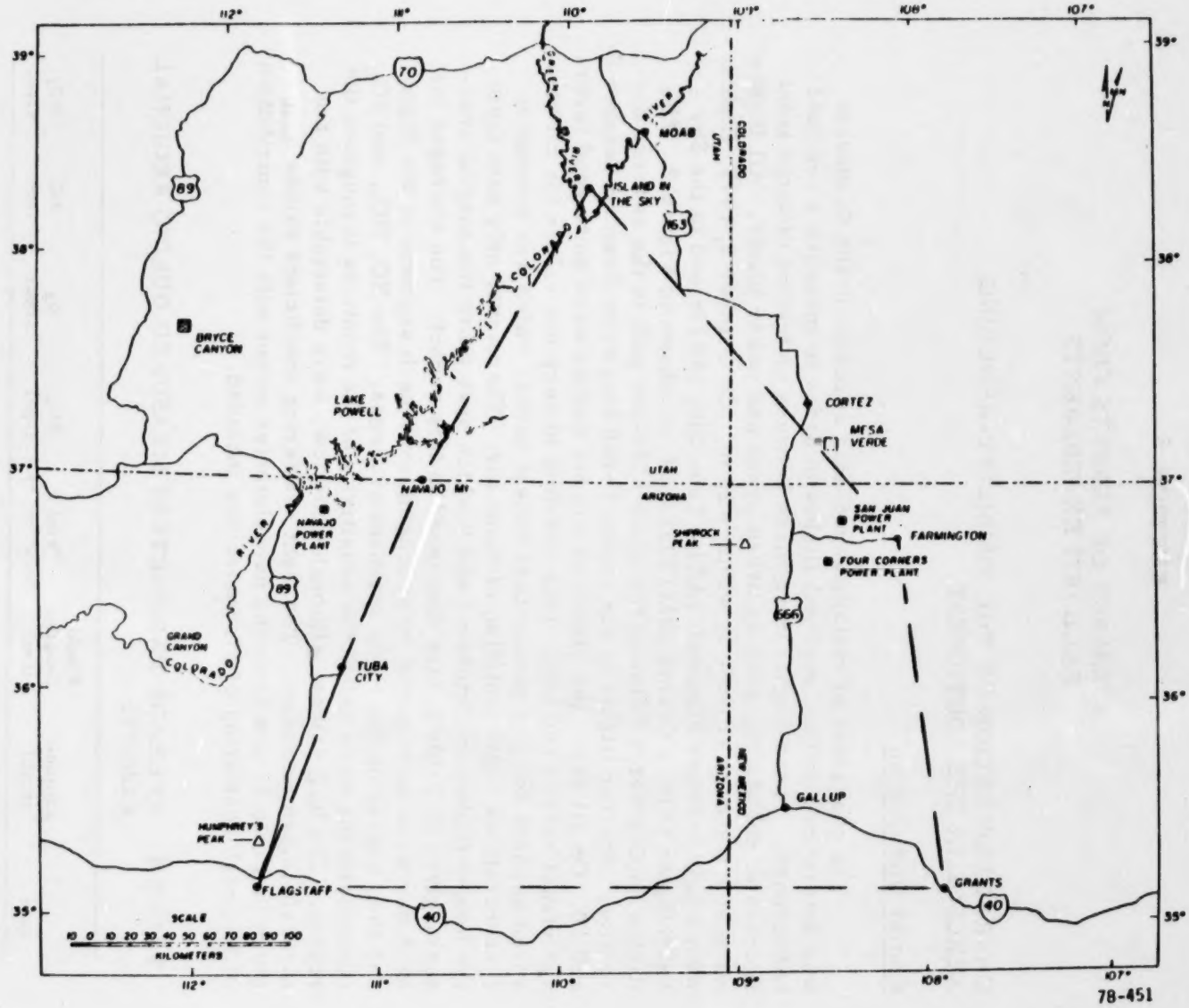

Figure 2. Flight path of VISTTA regional flights on October 5 and 9, 1977. The entire flight path is ~ 1080 km.

The spatial distribution of the visibility-reducing aerosol is most easily determined from the frequency distribution of the light-scattering coefficient due to particles, b_{sp}, as shown in Figure 3. These values are determined from the 10-sec average nephelometer readings with the Rayleigh scattering contribution to the scattering coefficient at the flight altitude subtracted.

The average value of b_{sp} on both sampling days was rather low, ranging from $(25 \pm 1) \times 10^{-6} m^{-1}$ on October 9 to $(28 \pm 3) \times 10^{-6} m^{-1}$ on October 5. Although these values are low, they are above the minimum sensitivity of the instrument [$b_{sp}(min) \cong 5 \times 10^{-6} m^{-1}$]. The Rayleigh scattering or clean air contribution at the sampling altitude ($\sim 11 \times 10^{-6} m^{-1}$) was, on the average, 42 percent of the total light scattering coefficient, during the very clear days on which these regional flights were made. The average measured visual range in-Mesa Verde and other national parks in the region in 1976 (Latimer et al., 1976) was about equal to the average visual range calculated from the scattering coefficient on the VISTTA sampling days (~150 km). Therefore, the VISTTA data can be considered typical for the region. The calculated visual range can be verified from photographs such as shown in Figure 4. Navajo Mountain, which is at a distance of 110 km, can be seen near the horizon in the photo. This photo was taken with a 50-mm Nikon lens, Kodachrome 64 film, and a UV filter. The ground elevation is ~2000 m msl, the aircraft is at 2429 m msl, and the mountain top is at 3166 m msl. The visual range calculated from b_{scat} measured along the sight path shown in Figure 4 was ~140 km.

The coefficient of variation of the b_{sp} frequency distribution was 7 percent on October 9 and 18 percent on October 5 over the entire 1080-km flight path, which indicates that the aerosol was homogeneous on both days.

Size Distribution

The average size distribution of background Southwest aerosol measured on the aircraft during the October 9 regional flight is shown in Figure 5. The distribution is bimodal. Reduction of the aerosol size distribution data was accomplished using reduction procedures described by Cantrell and Whitby, 1978. The size distribution data were collected every five minutes during the entire flight. All measured size distributions were averaged before extracting integral parameters using a lognormal approximation technique. There is some question about altitude effects on these instruments, which may lead to errors in the size distribution measurements. However, we do not think these errors are large enough to alter the conclusions of this report. We are presently looking into the magnitude of this

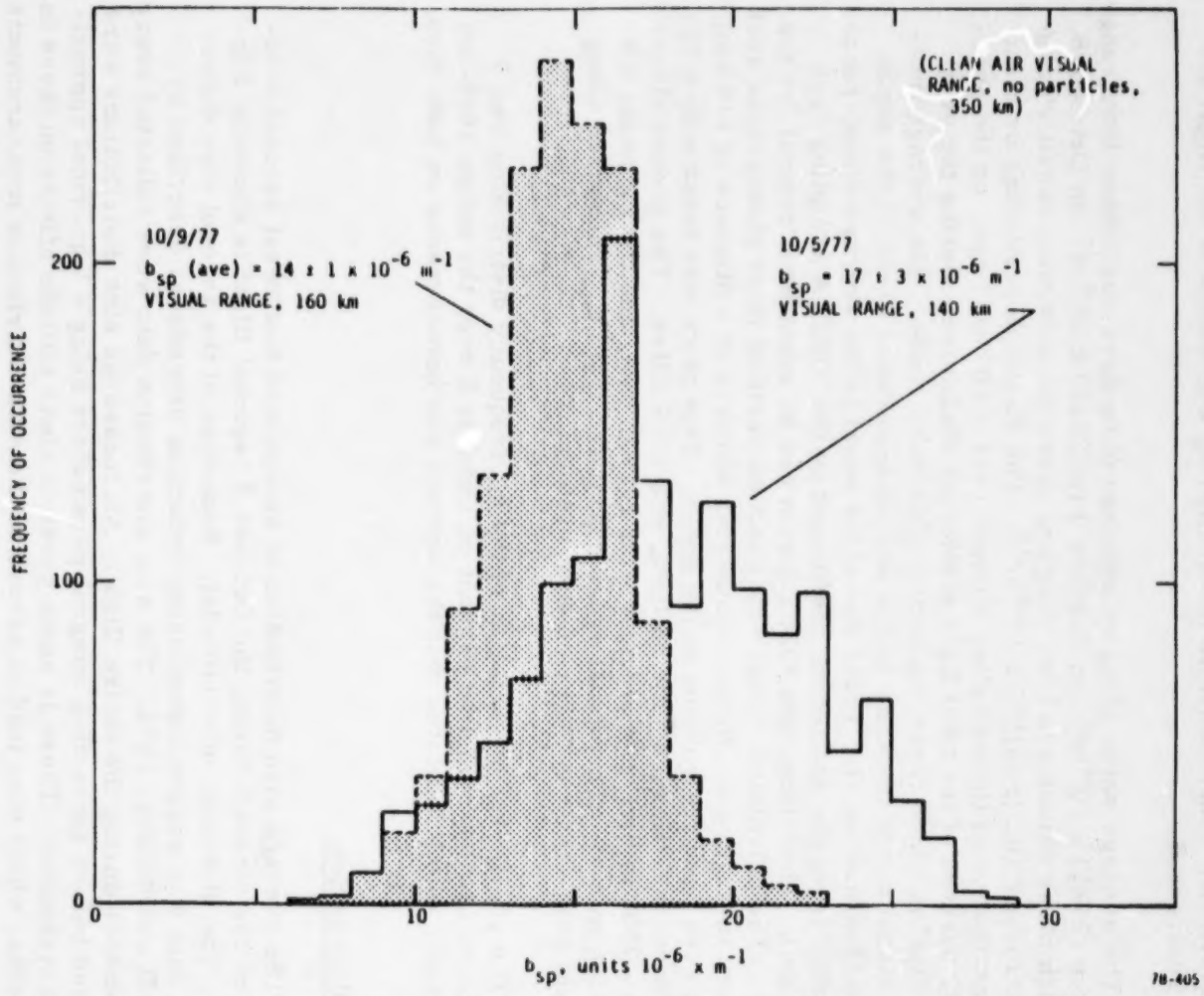

Figure 3. Frequency distribution of the light-scattering coefficient due to particles, b_{sp}, measured in regional flights on October 5 and 9, 1977. Measurements were averaged over 10 sec (1 km) for the 1080-km flight path for each day. The b_{sp} averages on October 5 and 9 were 17 and 14 x $10^{-6}m^{-1}$ with standard deviations of 3 and 1 x 10^{-6} m^{-1}, respectively, indicating that the aerosol was homogeneous on these days.

Figure 4. Photograph of Navajo mountain at a distance of 110 km from the aircraft of October 5, 1977. The visual range calculated from measured b_{scat} values along the sight path was ~140 km.

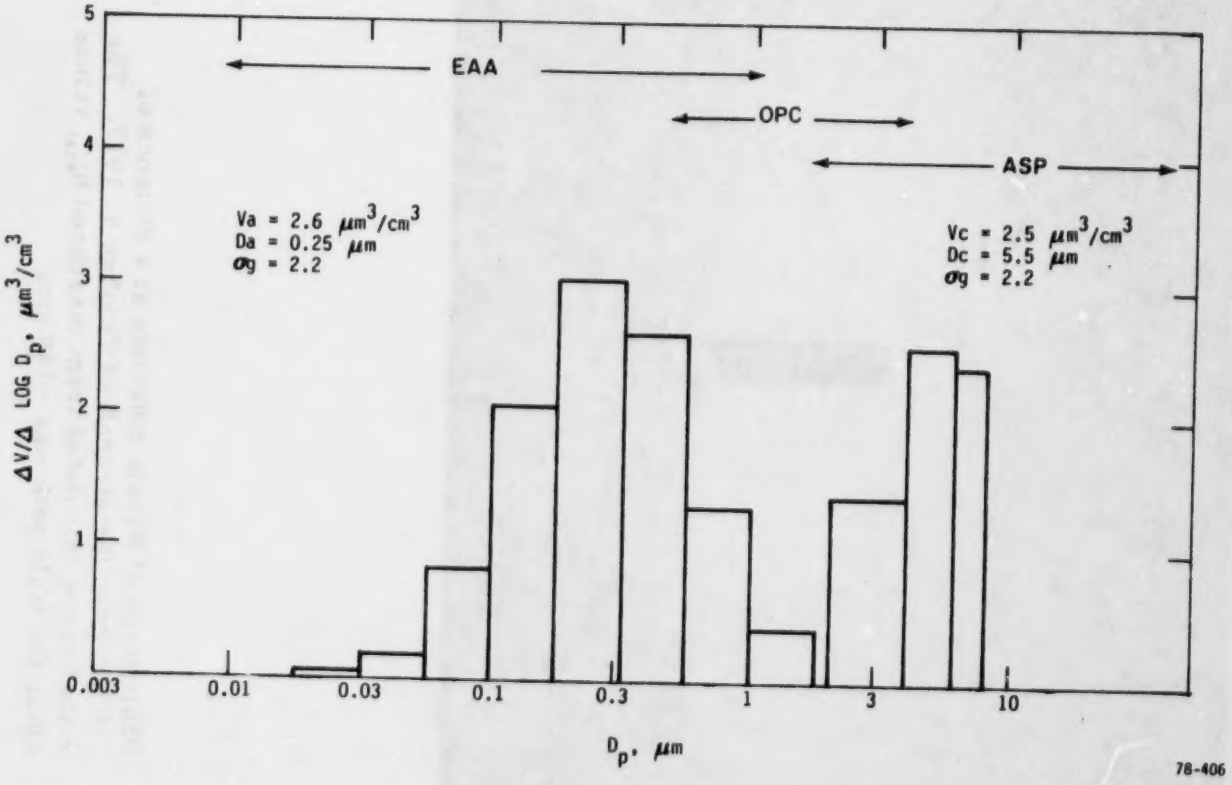

Figure 5. Average size distribution of background Southwest aerosol measured on the October 9, 1977, regional flight.

flow rate effect. The fine particle or accumulation mode had a geometric volume mean size, D_p, of 0.25 μm and a geometric standard deviation, σ_g, of 2.0. The coarse mode geometric volume mean size is 5.5 μm, with a σ_g of 2.2. The volume concentration of particles is 2.6 m^3/cm^3 and 2.5 m^3/cm^3 for the fine and coarse modes, respectively. The accumulation mode mean size is slightly smaller than the continental average of 0.3 μm described by Whitby (1978). However, the coarse particle mean size is the same as the continental average of 6 μm, within experimental error, expected for particles from similar sources such as windblown dust.

Elemental Composition

The elemental composition of the visibility-reducing aerosol in the Southwest was determined from impactor and filter samples collected on regional flights October 5 and 9, 1977. As discussed previously, the aerosol was quite homogeneous throughout the region during this sampling, making a regional average meaningful. The elemental concentrations divided into fine particles ($D_p \leq 1$ μm) and coarse particles ($D_p \geq 1$ μm) averaged for all samples collected on October 5 and 9 are given in Table 5. The rationale for the separation at 1 μm is based on the high scattering efficiency for particles with diameters less than 1 μm. Furthermore, particles in each of these size ranges generally have different chemical composition. All other elements not listed were below the minimum detectable limits. The elemental concentration of fine particle sulfur was measured by FV-FPD analysis of TWOMASS samples. All other data are from PIXE analysis of impactor samples. There was some discrepancy between the sulfur concentration values from the two techniques with the PIXE values being generally higher than the FV-FPD results. The explanation of this discrepancy is made more difficult because different samplers as well as different analysis techniques were used. In the second VISTTA study in Fall, 1978, additional samplers and sulfur analysis methods were used to get a more detailed understanding of this discrepancy and to obtain more reliable sulfur concentration values. In this report, the FV-FPD results were used in order to obtain preliminary conservative sulfur values. The detailed explanation of this problem will be given in a later VISTTA report. The coarse particle fraction is dominated by crustal elements such as silicon, aluminum, calcium, and iron. Sulfur, silicon, and potassium are predominant elemental species in the fine particles.

The size distribution of individual elemental species determined from regional impactor samples collected on the October 5 and 9 regional flights is shown in Figure 6. Aluminum, calcium, and iron all show very similar size distributions, with the highest concentration of each element in particles with diameters greater than 4 μm. The concentration on the final fil-

ter ($D_p \leq 0.5\,\mu m$) was below the minimum detectable limit for all these elements. Silicon has a size distribution similar to aluminum down to $1\,\mu m$; below that diameter the concentration of silicon increases. The concentration of small particle silicon ($D_p \leq 0.5\,\mu m$) is nearly equal to the large particle value ($D_p > 4\,\mu m$). These data indicate that silicon is a major contributor to the fine particle mass and, as discussed in a later section of this report, to visibility reduction. This is an unexpected but quite important result of this work. From the source characterization determined in this work, fine particle silicon is likely to be the result of condensation of volatile silicon emitted from high-temperature combustion sources. It is important to verify the presence of small particle silicon by further chemical measurements.

TABLE 5. AVERAGE ELEMENTAL CONCENTRATION OF AEROSOL IN THE SOUTHWEST REGION, OCTOBER 5 AND 9, 1977

Element[a]	Fine Particles[b] ($\mu g/m^3$)	Coarse Particles[c] ($\mu g/m^3$)
Al	0.01	0.28
Si	0.72	1.12
S	3.68	0.06
Cl	0.11	0.01
K	0.21	0.09
Ca	0.03	0.24
Ti	0.08	0.01
V	0.04	0.01
Cr	-	0.01
Fe	0.004	0.16
Zn	0.03	0.003
Zr	-	0.02
Pd	0.02	0.01
Ba	0.10	0.01
Pt	0.07	0.01
Pb	0.09	0.004

[a]The following elements were detected in only a few samples and, therefore, it is not possible to determine a meaningful average concentration:
Fine Particles - Cu, Mn, Ni, Rb, Co, Hg, Mo.
Coarse Particles - Cu, Mn, Se, Ni, Rb, Co, Mo, Br.

[b]Fine particle ($D_p \leq 1\,\mu m$) concentrations were determined from the sum of impactor stage 4 and the final filter. Sulfur values were determined from TWOMASS samples.

[c]Coarse particle ($D_p \geq 1\,\mu m$) concentrations were determined from the sum on impactor stages 1, 2, and 3.

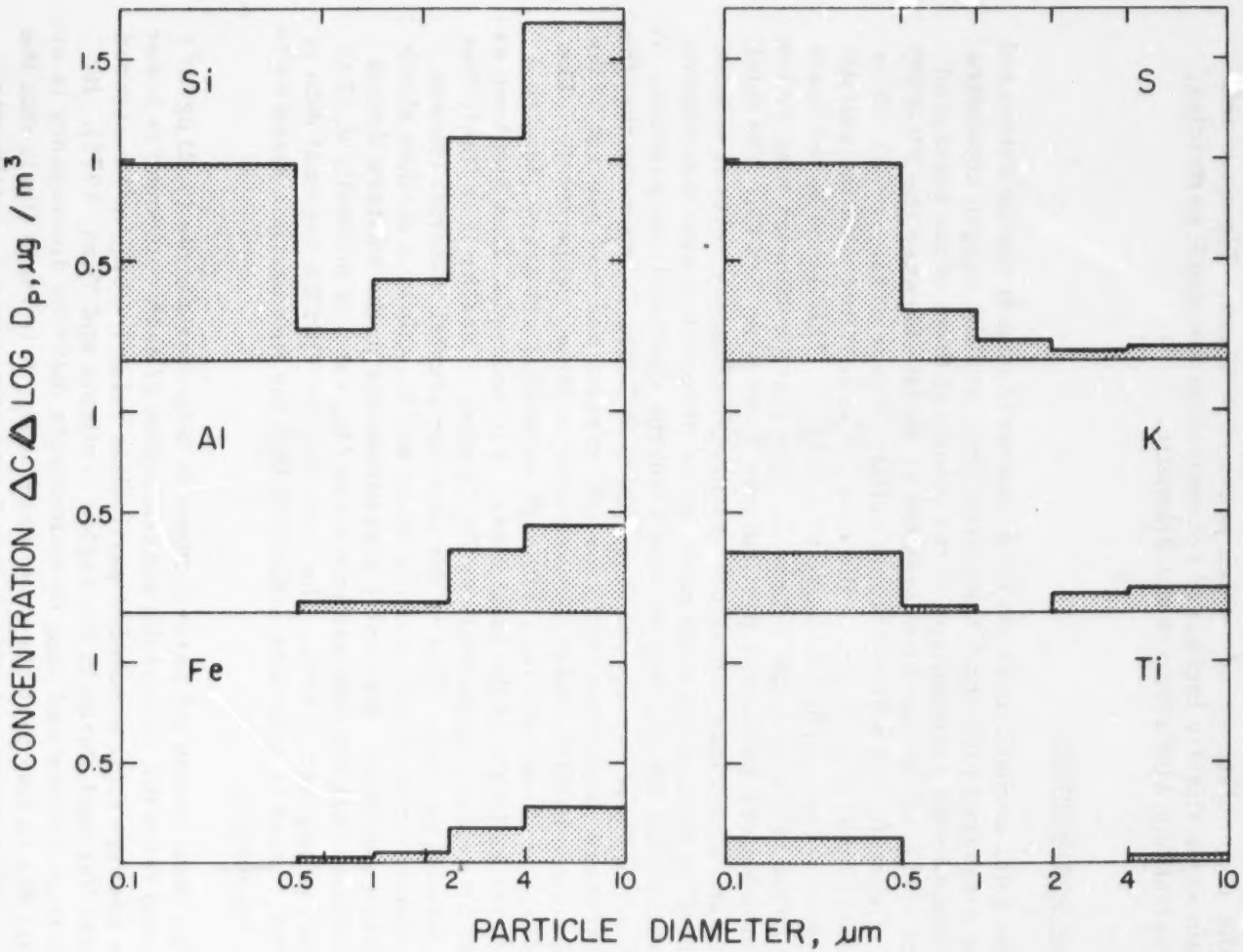

Figure 6. Average size distribution of individual elemental species determined from impactor samples collected on October 5 and 9 regional flights. Si has a size distribution similar to Al, Ca, and Fe down to 1 μm; below that diameter the concentration of Si increases.

Particulate sulfur is concentrated mainly in small particles ($D_p \leq 0.5\,\mu m$). This is reasonable considering that $SO_4^=$ is a large fraction of the accumulation mode which peaks at $0.25\,\mu m$. Titanium and potassium show slightly increased concentration for small partricles, but the variations with size are not dramatic.

Chemical Composition

The total aerosol mass was not measured, but it can be estimated from the measured elemental concentrations, and the oxygen concentration estimated with assumptions of the chemical form of the measured elements. The sulfur can be expressed as sulfate because the FV-FPD method is specific for water-soluble sulfate (Husar et al., 1975). It is also assumed that ammonium is the only ion associated with the sulfate. Other elements are assumed to exist as oxides. This leads to the mass balance listed in Table 6 and Figure 7. The mass estimates may be low due to unmeasured elements, particularly those with $Z < 13$. The total mass in each size range can also be estimated from the aerosol volume determined by integrating each mode in the differential size distribution and by estimating the aerosol density from the chemical composition. A comparison of these two approaches, given in Table 7 indicates that the elemental mass balance accounts for ~93 percent and ~64 percent of the fine and coarse particle mass derived from volume, respectively. The assumptions of chemical form, although somewhat arbitrary, lead to a conservative estimate of the total mass. For example, iron has been assumed to be present exclusively as Fe_2O_3 when in reality it is likely that FeO is present as well. This is the case for crustal material (Mason, 1966). Comparison of fine particle mass and b_{sp} allows a further check on the mass estimate. Extensive measurements in the western United States indicate that the fine particle mass / b_{sp} ratio is normally 0.32 to $0.34\ g/m^2$ (Waggoner, 1978). The ratio for the VISTTA regional data is $0.34\ g/m^2$, which is a further indication that the fine particle mass estimate is reasonable.

The total measured aerosol mass in both size ranges ($9.23\,\mu g/m^3$) determined from the sum of the concentration of each compound is lower than the average total suspended particulate value ($\sim 20\,\mu g/m^3$) measured in several National Parks in the region (Trijonis and Yuan, 1978). It appears from volume and b_{scat} measurements that this discrepancy is not primarily due to fine particle mass estimates. It is more likely that the coarse particle mass estimate is low due to unmeasured constituents. Furthermore, coarse particles may be diminished due to settling at 300 to 500 m above the ground where the samples were collected.

TABLE 6. CHEMICAL SPECIES BALANCE FOR THE SOUTHWEST REGION– OCTOBER 5 AND 9, 1977

Compound	Fine Particles		Coarse Particles	
	Concentration ($\mu g/m^3$)	Contribution[a] (%)	Concentration ($\mu g/m^3$)	Contribution (%)
Al_2O_3	0.02	0.4	0.53	13.4
SiO_2	1.54	29.2	2.40	60.6
$(NH_4)_2SO_4$	2.81	53.3	0.25	6.3
K	0.21	4.0	0.09	2.3
CaO	0.04	0.8	0.34	8.6
TiO_2	0.13	2.5	0.02	0.5
Fe_2O_3	0.006	0.1	0.23	5.8
ZnO	0.04	0.8	0.004	0.1
PbO	0.10	1.9	0.004	0.1
Other (in normal oxide form)	0.37	7.0	0.09	2.3
Total	5.27	100.0	3.96	100.0

[a] - The percent contribution is based on the mass estimated from the sum of the chemical concentrations.

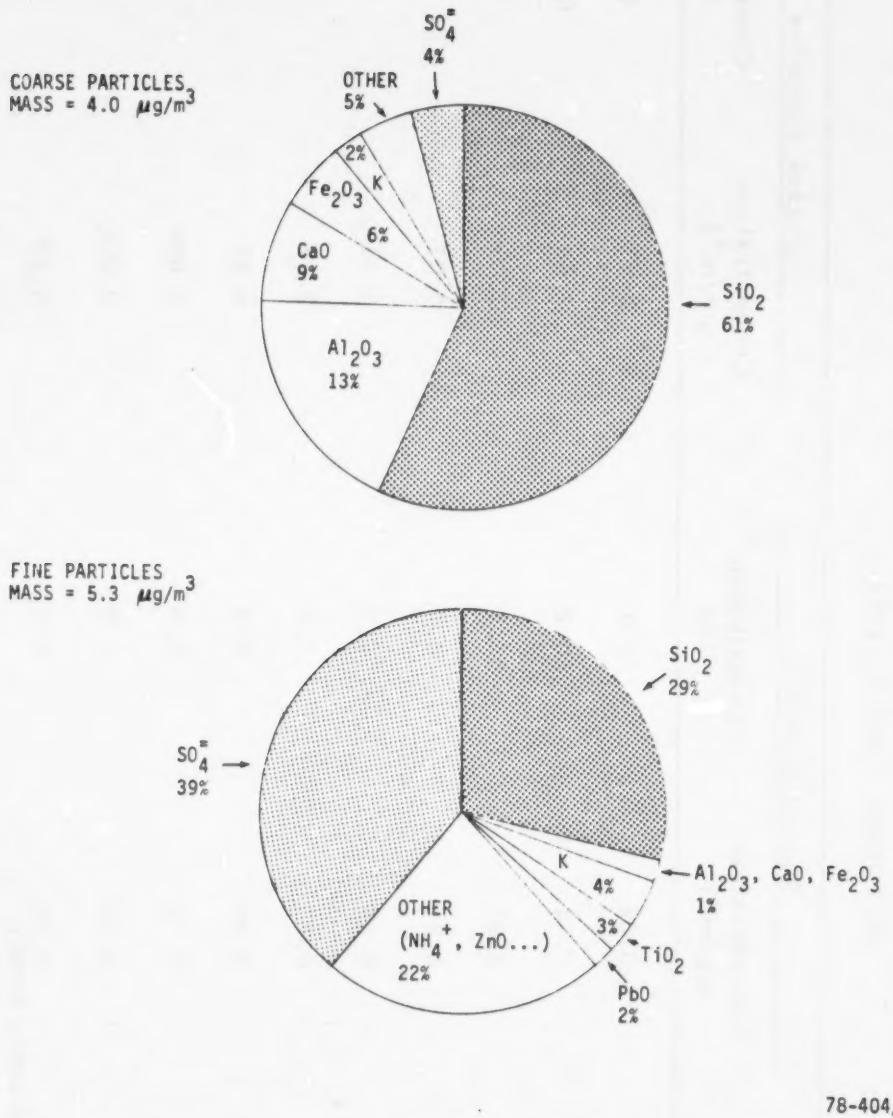

Figure 7. Size-fractioned mass balance of Southwest background aerosol measured on regional flights on October 5 and 9, 1977. The concentration of individual compounds was determined from the measured elemental concentration and assumed chemical form. The total aerosol mass in each size fraction was determined from the sum of the individual chemical components. Comparison with aerosol volume measurements indicates that the mass estimated from composition measurements represents 93% and 64% of the fine and coarse particle mass, respectively.

TABLE 7. COMPARISON OF AEROSOL MASS DETERMINATIONS FROM VOLUME AND COMPOSITION MEASUREMENTS

	Aerosol Volume Measurements			Aerosol Composition Measurements	
Particle Type	Volume ($\mu m^3/cm^3$)	Mass Weighted Density Estimate (g/cm^3)	Mass Derived from Volume ($\mu g/m^3$)	Mass Derived from Composition ($\mu g/m^3$)	Composition-Derived Mass Relative to Volume-Derived Mass (percent)
Fine ($D_p \leq 1\mu m$)	2.6	2.2	5.7	5.3	93
Coarse ($D_p \geq 1\mu m$)	2.5	2.5	6.2	4.0	64

Probably the most important species unaccounted for are nitrates, carbon compounds, and water. The average annual concentration of nitrate in the nonurban Southwest region was about 20 percent of the sulfate value in the early 1970's as measured in Grand Canyon and other remote Southwestern national parks by the National Air Surveillance Network (Latimer et al., 1978). These values may be subject to error due to artifact sulfate and nitrate effects on filters. Very few data exist on the concentration of carbon in Southwest ambient aerosols, but it is a significant component of eastern urban aerosols (Lewis and Macias, 1978).

Enrichment Factors

The predominant species in the coarse particles are elements found in high concentration in soil and crustal material. Elemental enrichment factors, given in Table 8, help to characterize the source of these particles. These factors are calculated as follows:

$$\text{Enrichment Factor (EF)} = \frac{(X/Al)\ \text{Aerosol}}{(X/Al)\ \text{Crust}} .$$

TABLE 8. SOUTHWEST REGIONAL AEROSOL ENRICHMENT FACTORS

Element	Enrichment Factor: Fine Particles ($D_p \leq 1\ \mu m$)		Enrichment Factor: Coarse Particles ($D_p \geq 1\ \mu m$)	
Al	1.0	Crustal Abundance	1.0	Crustal Abundance
Fe	0.7		0.9	
Si	21		1.2	
K	66		1.0	
Ca	7		1.9	
Ti	1×10^2		0.7	
S	2×10^4	Enriched Relative to Crust	67	Enriched Relative to Crust
Cl	7×10^3		23	
V	2×10^3		29	
Cr	-		13	
Zn	4×10^3		35	
Zr	-		3×10^5	
Pd	2×10^7		7	
Ba	2×10^3		3×10^5	
Pt	6×10^7		88	
Pb	6×10^4			

Aluminum was chosen as the reference element because its major source is likely to be soil. However, aluminum is also present in flyash from coal combustion (Lyon, 1977). Crustal abundances were taken from Mason (1976). Enrichment factors >1 indicate an enrichment of that element relative to crustal abundances; values <1 indicate a depletion relative to crust. Because of the uncertainty in the data, EF values between 0.5 and 2 indicate no significant difference from crustal abundance. It can be seen from Table 8, that Si, K, Ca, Ti, V, and Fe are all near the crustal abundance in the coarse particles relative to Al. These elements represent 93 percent of the measured coarse particle mass. The other coarse particle species are enriched, indicating an anthropogenic source. This analysis is complicated by the fact that many of these elements are present in coal flyash with abundances similar to crustal material.

All fine particle species except iron are enriched relative to the crust (normalized to aluminum) with enrichment factors ranging from 7 to 2×10^7. The enriched fine particle species represent 99.5 percent of the measured fine particle mass, which indicates that the vast majority of fine particles are not due to wind-blown dust of crustal origin.

Light Scattering Budget

The detailed contributions to light scattering as a function of particle size can be determined from Mie calculations (Mie, 1908) of the light scattering efficiency and the measured particle size distribution. The sum of the calculated b_{sp} over all particle sizes can be compared to the measured light scattering coefficient from the integrating nephelometer. Mie scattering calculations combined with particle size and composition measurements permit the determination of the individual contribution to visibility reduction for particles of a given composition and size (light scattering budget). This approach can also serve as a test of the consistency of the various measurements. Ensor et al. (1972) have described the calculations used in this work in an earlier paper. The following expression was evaluated in the scattering coefficient calculation:

$$b_{scat} = \int G(D_p) \frac{dV}{d \log D_p} d \log D_p \ ,$$

where G is the light scattering per unit volume of aerosol. The quantity G, calculated using Mie scattering functions, is plotted in Figure 8 as a function of particle size for a refractive index m = 1.54 and a standard solar radiation distribution at sea level. It can be seen from the figure that particles with diameters between 0.1 and 1 μm have the greatest scattering efficiency.

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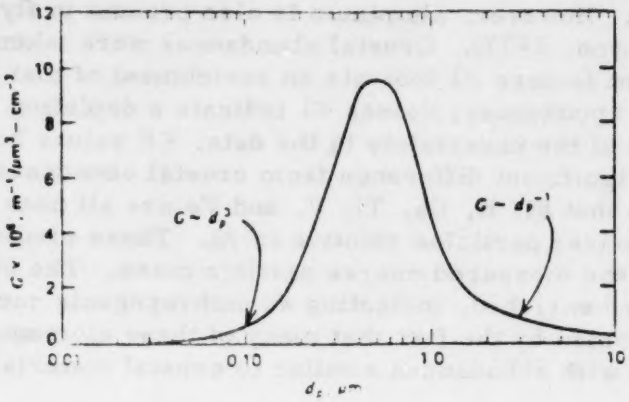

Figure 8. Light scattering per unit volume of aerosol material as a function of particle size, integrated over all wavelengths for a refractive index, m = 1.5. The incident radiation is assumed to have the standard distribution of solar radiation at sea level (Bolz, R. E., and Tuve, G. E. (Eds.), 1970, Handbook of Tables for Applied Engineering Science, Chemical Rubber Co. Cleveland, Chio, p. 159.) The limits of integration on wavelength were 0.36 to 0.680 μm. The limits of visible light are approximately 0.350 to 0.700 μm. (Friedlander, 1977)

The contributions to the light scattering coefficient as a function of particle size for the average Southwest regional aerosol (October 9, 1977) calculated from the average regional aerosol size distribution are given in Figure 9. A refractive index, m = 1.54, was used in this calculation, which is slightly lower than the mass-weighted values of 1.57 and 1.65 for fine and coarse particles, respectively, calculated from aerosol composition measurements. The calculation was done for light of 525 nm wavelength. The sum over all calculated contributions yields

$$\sum b_{sp} = (16 \pm 2) \times 10^{-6} m^{-1} ,$$

which agrees well with the average value of light scattering due to particles measured with the integrating nephelometer (with the contribution of Rayleigh scattering due to gases removed) of $b_{sp}(\text{measured}) = 14 \pm 1 \times 10^{-6} m^{-1}$

The visibility budget for the Southwest background aerosol on October 9, 1977, determined from the Mie calculations, indicates that 52 percent of the light scattering was due to fine particles ($D_p \leq 1 \mu m$), 44 percent was due to Rayleigh scattering from gases, and 4 percent was due to coarse particles. Considering only the light scattering due to particles, 93 percent is due to fine particles. The detailed visibility budget, summarized in Table 9, was constructed using the results of the fine particle mass balance and assumes that sulfur and silicon compounds have the same size distribution as the total fine particle aerosol. This is reasonable, since these compounds represent 82 percent of the measured fine particle mass.

TABLE 9. LIGHT SCATTERING BUDGET FOR THE SOUTHWEST REGION OCTOBER 9, 1977 (Visual Range ~160 km)

Component	D_p (μm)	b_{scat} ($\times 10^{-6} m^{-1}$)	Contribution to Total b_{scat} (percent)
Air Molecules	---	11	44
$(NH_4)_2SO_4$ [a]	0.1 to 1.0	7	28
SiO_2 [b]	0.1 to 1.0	4	16
Other Compounds	0.1 to 1.0	2	8
Coarse Paricles (Given in Table 5)	1.0 to 20.0	1	4
		25 $\times 10^{-6} m^{-1}$	100

[a] Assumes that all fine particle sulfate exists as ammonium sulfate.

[b] Assumes that all fine particle silicon exists as SiO_2.

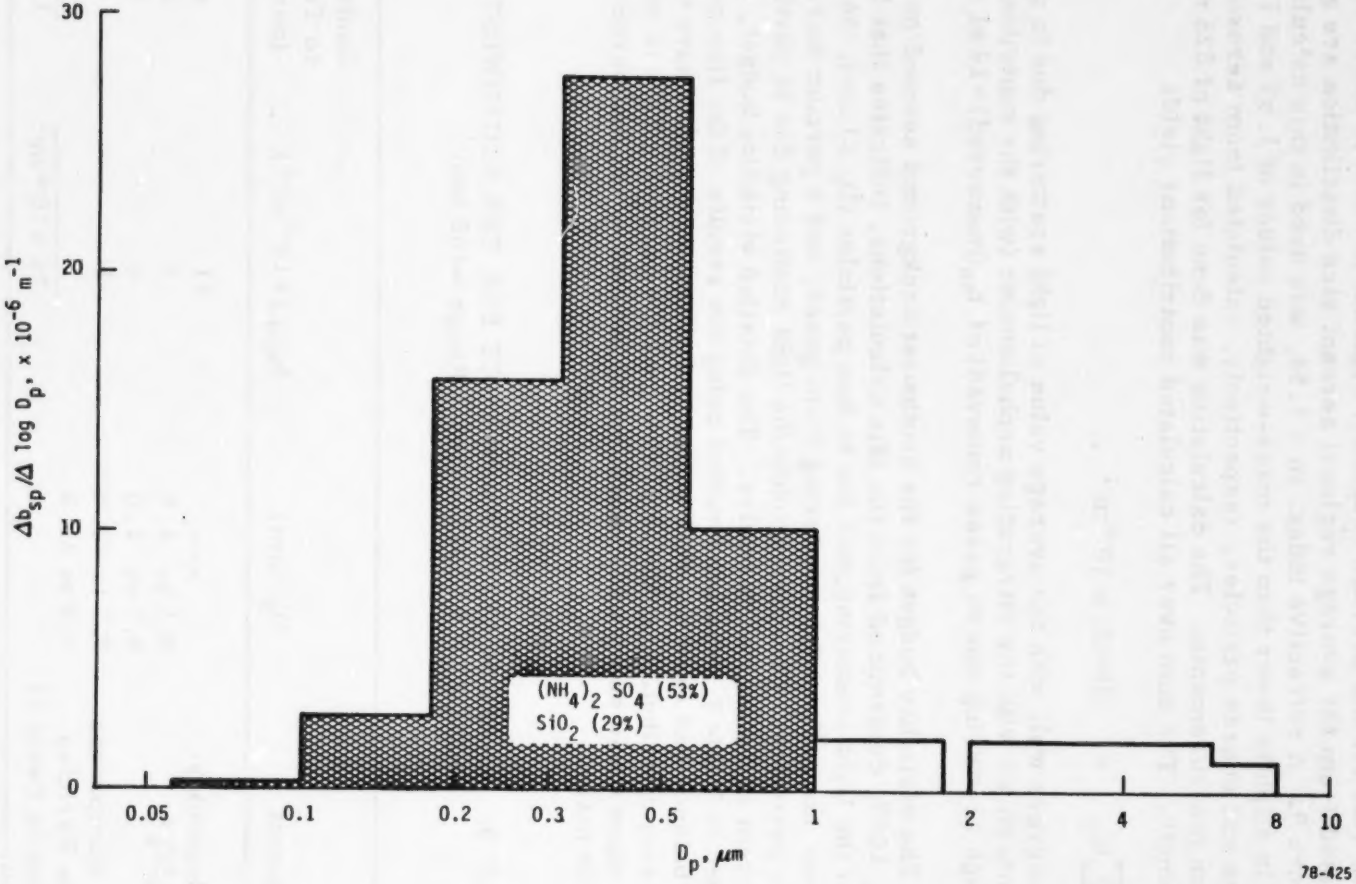

Figure 9. Light scattering contribution as a function of size for the Southwest region, October 9, 1977. The fine particle contribution, which represents 93% of the total b_{sp}, is shaded in the figure.

The ratio of fine particle sulfate mass to the total b_{sp} value for the Southwest region measured on October 9, 1977, is 0.15 g($SO_4^=$)/m^2. A similar calculation for the fine particle SiO_2 mass / b_{sp} ratio yields 0.11 g(SiO_2)/m^2. Perhaps a more interesting calculation is the ratio of fine particle sulfate or SiO_2 mass to the contribution of that species to b_{sp}, as determined in the visibility budget. This ratio is 0.4 g/m^2 for for both fine particle sulfate and SiO_2.* This calculation assumes that sulfur and silicon have the same size distribution.

SOURCE CHARACTERIZATION

In order to characterize the emissions from specific sources in the region, measurements were made in plumes from the San Manuel copper smelter on October 1, 2, and 4, 1977, and the Mohave power plant October 8, 1977. The flight paths on these days are shown in Figures 10 and 11. Separate orbital flights in the plume and in the background, as well as plume traverses, were carried out at each distance downwind of the source as outlined in Table 2. Analog gas and aerosol parameters measured during these flights averaged over each flight segment are summarized in Table 10. Data from October 1 have not been included in Table 10 or in any subsequent data analysis because of the poor spatial resolution of the plume on that day. A photo of the San Manuel smelter plume 8 km downwind of the plant looking normal to the plume is shown in Figure 12. The plume is easily visible and well defined against the sky and mountains.

To help evaluate the data presented in this section on source characterization it is instructive to compare the emission rates of the San Manuel smelter and Mohave power plant. In 1975 the Mohave power plant emitted an estimated average of 66 tons/days of SO_x and 77 tons/day of NO_x (Marians and Trijonis, 1978). In 1977 the San Manuel smelter emitted 557 tons per day of sulfur, expressed as SO_2 (Larson and Billings, 1978).

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* - The inverse of this ratio, i.e., the contribution of $SO_4^=$ or SiO_2 to b_{sp} divided by the fine particle $SO_4^=$ or SiO_2 mass is $\frac{2.5 \times 10^{-6} m^{-1}}{\mu g/m^3}$ for SO_4 and for SiO_2.

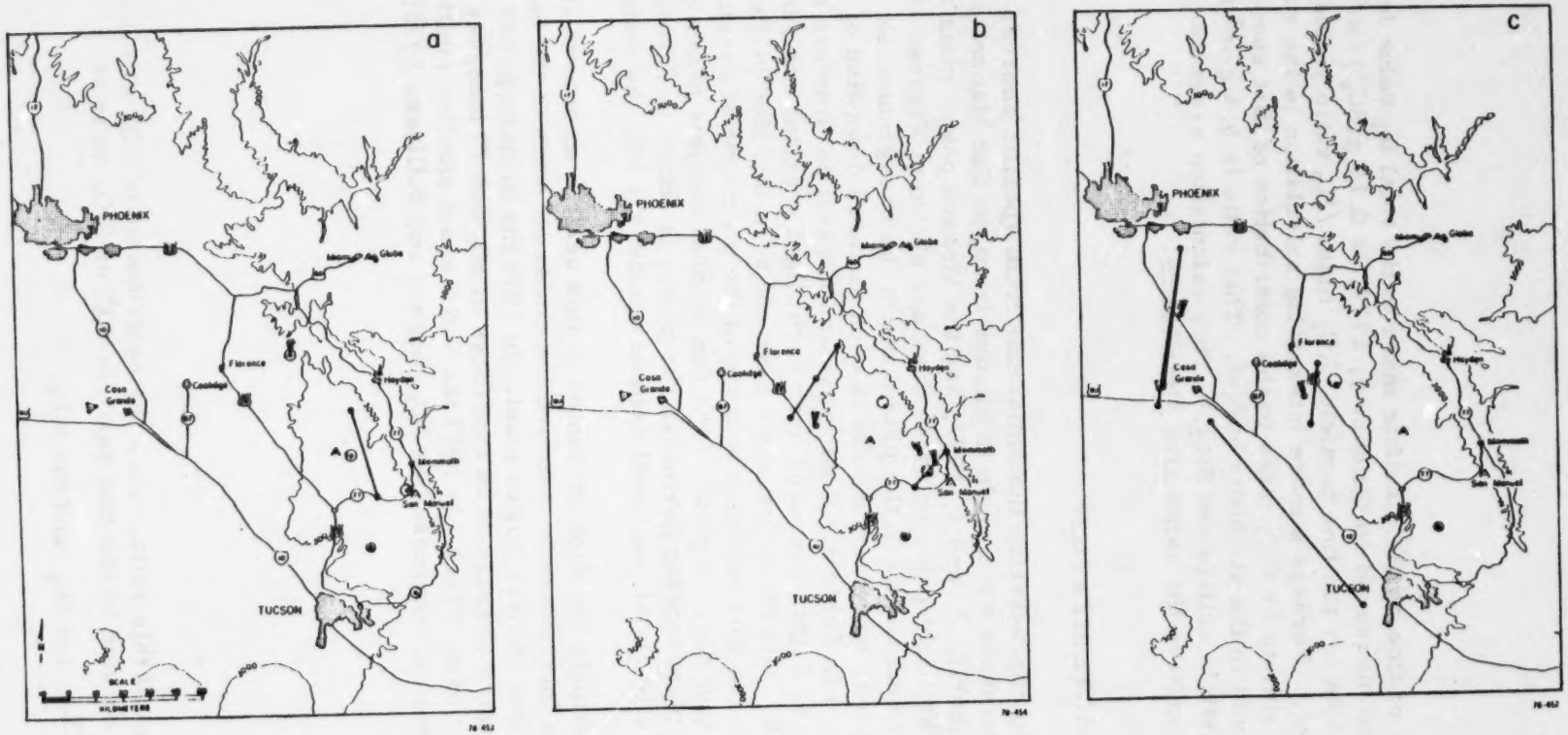


Figure 10. Flight map of Arizona smelter flights on (a) October 1, 1977, (b) October 2, 1977, and (c) October 4, 1977.

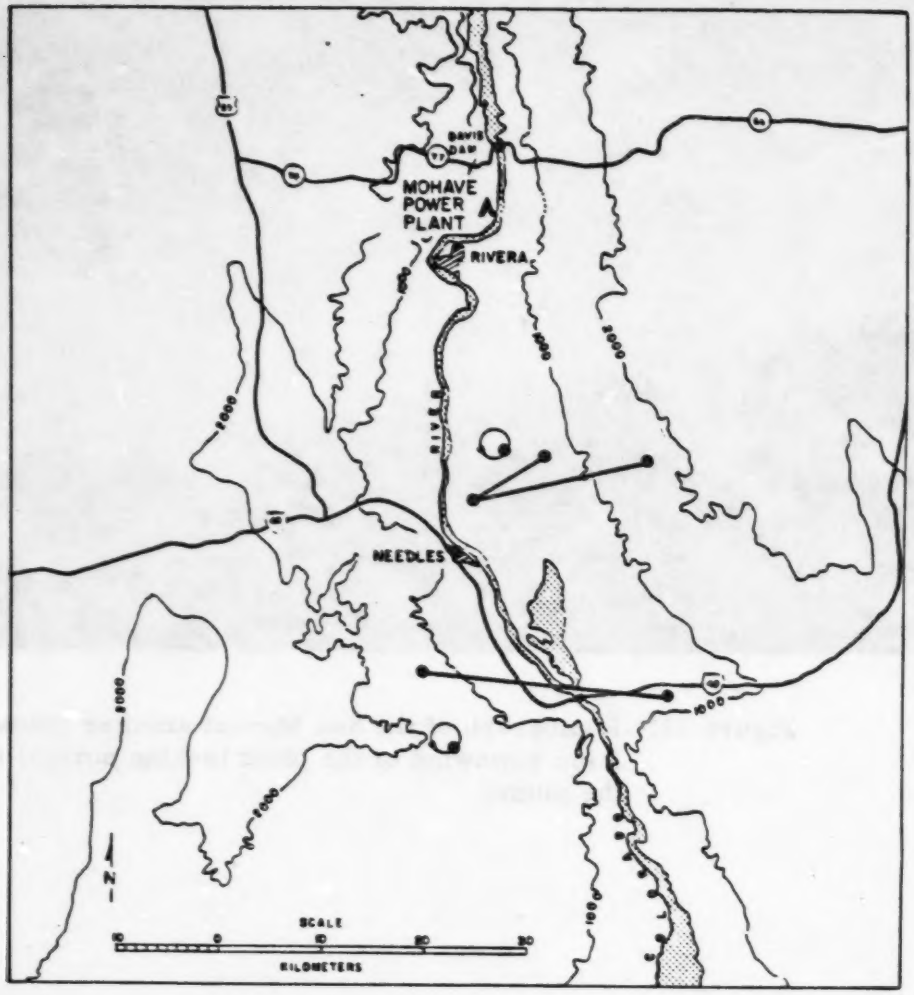


Figure 11. Flight map of Mohave power plant flights on October 8, 1977.

Figure 12. Photograph of the San Manuel smelter plume 8 km downwind of the plant looking normal to the plume.

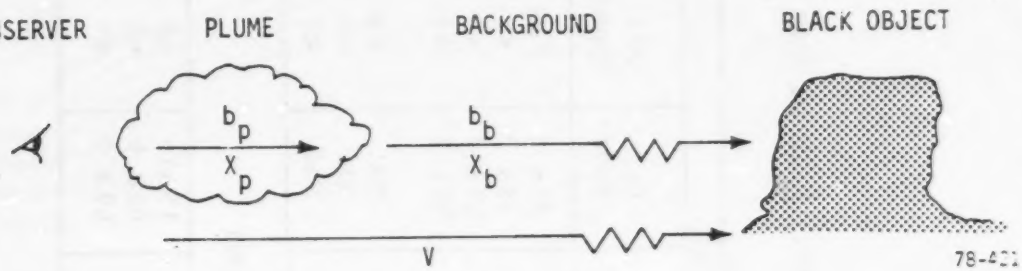
TABLE 10. AVERAGE PARAMETERS MEASURED DURING CRBIT PLUME FLIGHTS

Date	Distance Downwind (km)	Altitude (msl)	b_{scat} ($10^{-6}m^{-1}$)	SO_2 (ppb)	O_3 (ppb)	NO (ppb)	NO_x (ppb)
SAN MANUEL SMELTER							
10/2/77	8	1,220±19	329±86	653±254	55± 3	5±2	5±1
	32	1,066±25	138±93	86±110	58± 3	<5	<5
	60	1,206±70	128±22	57± 10	63± 4	<5	<5
	Bkgrnd	1,214±33	46± 8	19± 4	49± 3	<5	<5
10/4/77	60	907±14	128±41	78± 30	NM	<5	<5
	127	452±16	83±11	32± 10	NM	<5	<5
	Bkgrnd	1,026±24	33± 3	7± 3	NM	<5	<5
MOHAVE POWER PLANT							
10/8/77	32	670±15	54±22	5± 8	15±15	<5	19±10
	62	670±12	69±12	2± 1	65± 6	<5	16± 5
	Bkgrnd	924±23	36± 2	0.9 ±0.3	69± 2	<5	5± 2

NM = no measurement of O_3 on 10/4/77

Plume Impact

The impact of a plume on visibility can be estimated by comparing the visual range with the plume present to the visual range through the background without the plume. The parameters used in this semi-quantitative calculation are shown in the schematic diagram below.



The subscripts p and b indicate plume and background parameters, respectively. The light scattering coefficient in the plume, b_p, includes the background contribution.

The visual range, V, is defined as "the distance, under daylight conditions, at which the apparent contrast between a specified type of target and its background becomes just equal to the threshold contrast of an observer" (Huschke, 1959). For the following analysis, the target and background are a black object viewed against the horizon sky, and the threshold contrast of a typical observer, 0.02, is used (Middleton, 1952). In this case, the visual range is given by

$$V = \frac{-\ln 0.02}{\overline{b_{ext}}} = \frac{3.9}{\overline{b_{ext}}},$$

where $\overline{b_{ext}}$ is the average extinction coefficient along the sight path. This equation assumes uniform illumination along the sight path, and neglects multiple scattering.

The following calculations assume that the contribution of absorption to extinction is small, so that the equation for visual range can be rewritten as $V\overline{b_{scat}} = 3.9$. For the case depicted above of a plume imbedded in background air, the corresponding equation is $X_p b_p + X_b b_b = 3.9$, where b_b and b_p are the average scattering coefficients in the background and plume, respectively, and X_p is the measured plume width. The quantity $X_p b_p$, termed the optical depth of the plume (τ_p), is the integral of scattering across the plume, i.e.,

$$\tau_p = \int b_p(x)\,dx.$$

The visual range looking through the plume was calculated using the equation

$$V = X_p + X_b = X_p + \frac{3.9 - \tau_p}{b_b} .$$

The values for X_p, b_p, and b_b were determined from measurements at the the lowest altitude at which plume traverses were made. The plume opacity is defined in terms of the plume optical depth as $1 - \exp(-\tau)$.

The visual range and plume optics calculations are summarized in Table 11 and Figure 13. The visual range through the copper smelter plume is reduced at 8 km downwind of the stack from 135 km in the background to 13 km with the plume present (90 percent reduction). The visibility reduction decreases further downwind of the plant. At 60 km downwind, the visual range is 82 km with the plume present (39 percent visibility reduction relative to the background). The visibility reduction with the plume present is nearly equal at 60 and 127 km downwind of the smelter. The power plant plume exhibits quite different visual behavior.

TABLE 11. PLUME IMPACT DATA

	Downwind Distance (km)	Plume Width (km)	Plume Optical Depth	Plume Opacity	Visual Range With Plume (km)	Visual Range Background	Visual Range Reduction due to Plume (%)
San Manuel Smelter	8	16	4.9	0.99	12	135	90
	32[a]	20	2.8	0.94	54	135	60
	60	25	2.2	0.89	82	135	39
	127	54	3.1	0.95	78	135	42
Mohave Power Plant	32	8	0.66	0.48	98	110	11
	60	27	1.92	0.85	82	110	25

[a]Plume width at 32 km downwind interpolated from measurements at 8 and 60 km downwind.

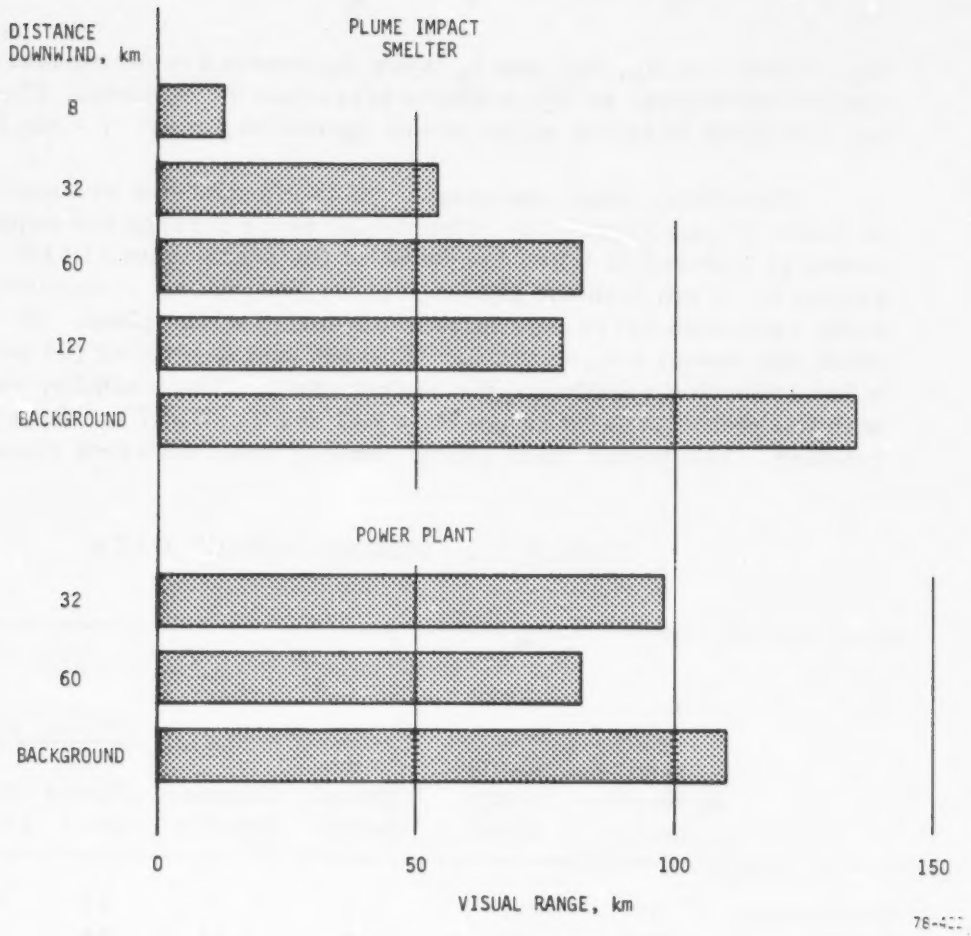


Figure 13. Visual range calculations for the smelter and power plant at several distances downwind compared to the background visual range.

The reduction of the background visual range is less at 32 km than at 60 km downwind (11 percent versus 25 percent, respectively). However, the power plant plume was measured under meteorological conditions which varied during the day, resulting in erratic plume behavior. The difference in the reduction of the background visual range between these plumes may be the result of greater emissions released from the smelter stack and of greater dispersion of the Mohave plume on October 8.

Elemental Composition in Plumes

The elemental composition of the plume excess aerosol, i.e., the plume aerosol with the background subtracted, was determined from the analysis of samples collected in orbital plume flights. The background concentrations were determined in orbital flights upwind of the plume. The aerosol elemental composition for the San Manuel smelter plume at 60 km downwind and the Mohave power plant at 32 km downwind are given in Table 12.

TABLE 12. PLUME EXCESS* AEROSOL ELEMENTAL CONCENTRATION

	San Manuel Smelter 60 km downwind (10/4/77)		Mohave Power Plant 32 km downwind (10/8/77)	
Element[a]	Fine Particles[b] ($\mu g/m^3$)	Coarse Particles[c] ($\mu g/m^3$)	Fine Particles ($\mu g/m^3$)	Coarse Particles ($\mu g/m^3$)
Al	<0.01	1.91	0.05	1.46
Si	1.08	6.12	0.34	3.67
S	2.29	-	0.30	-
K	0.43	0.60	-	0.25
Ca	-	1.58	-	1.16
Ti	0.02	0.03	-	0.04
Mn	-	0.02	-	-
Cr	0.20	0.06	-	0.05
Fe	0.02	1.02	-	0.55
Cu	-	0.06	-	-
Ni	-	-	0.20	0.01
Se	0.26	-	-	-
Pb	-	-	-	0.03

[a] Molybdenum was detected in concentrations above background but at the minimum detectable limit in the Mohave power plant plume.

[b] Fine particle ($D_p \leq 1\mu m$) concentrations were determined from the sum of impactor stage 4 and the final filter. Sulfur values were determined from TWOMASS samples.

[c] Coarse particle ($D_p \geq 1\mu m$) concentrations were determined from the sum of impactor stages 1, 2, and 3.

* - Plume excess values were determined by subtracting background concentrations from plume concentrations of each element.

The largest plume excess elemental constituents of the fine particle aerosol in both plumes are sulfur and silicon. Silicon, aluminum, calcium, and iron are major constituents of the plume excess coarse particles. These data indicate that coal-fired power plants and copper smelters in the Southwest may be major sources of the fine particle silicon as as well as sulfur, the two major consitutents of the Southwest visibility-reducing aerosol.

Plume excess aerosol enrichment factors for the San Manuel smelter and Mohave power plant are given in Table 13. Coarse particle Si, K, Ca, Ti, and Fe in both plumes and coarse particle Mn in the smelter plume are present in crustal abundances relative to Al. Thus, the crustal abundances of these elements in Southwest background coarse particles may be an indication that the source of these particles is crustal weathering or flyash. Plume excess coarse particle Cr, Ni, Cu, and Pb are all enriched relative to crustal abundances. All plume excess fine particle species are enriched relative to the crust except for fine particle Si in the Mohave plume.

The size distribution of plume excess elemental constituents shows many similarities with the regional data. Aluminum, calcium, and iron all exhibit the highest concentrations for particles with diameters >4μm. Silicon has a size distribution similar to aluminum down to 1μm but increases below that diameter. Sulfur is mainly concentrated in fine particles.

TABLE 13. PLUME EXCESS AEROSOL ENRICHMENT FACTORS

Element	San Manuel Smelter 60 km downwind (10/4/77) Fine Particles	Coarse Particles	Mohave Power Plant 32 km downwind (10/8/77) Fine Particles	Coarse Particles
Elements in crustal abundances in coarse particles, enriched in fine particles				
Al	1.0	1.0	1.0	1.0
Si	32	0.9	2	0.7
K	1×10^2	1.0	-	0.5
Ca	-	2	-	2
Ti	37	0.3	-	0.5
Mn	-	0.9	-	-
Fe	3	0.9	-	0.6
Elements enriched in both size fractions				
S	7×10^4	-	2×10^3	-
Cr	2×10^4	26	-	28
Ni	-	-	4×10^3	7
Cu	-	46	-	
Se	4×10^7	-	-	
Pb	-	-	-	128

The total aerosol mass was not measured but can be estimated from the elemental concentrations and mean aerosol volume as described previously. A comparison of these two approaches shows that in the San Manuel smelter on October 4, 1977, at 62 km downwind, 100 percent of the plume excess fine particle mass determined from plume excess aerosol volume (assuming a mass weighted density of 2 g/cm^2) can be accounted for from the measured constituents. The coarse particle volume was not measured in this plume. Approximately 73 percent of the plume excess fine particle mass is sulfate (expressed as ammonium sulfate), and 17 percent is silicon (expressed as SiO_2). In the Mohave power plant plume on October 8, 1977, only about 50 percent of the fine particle mass determined from aerosol volume can be accounted for by the measured constituents. Of this 50 percent at 32 km downwind, plume excess sulfate [expressed as $(NH_4)_2SO_4$] accounts for 52 percent of the mass inferred from measured aerosol composition and plume excess fine particle silicon (expressed as SiO_2) accounts for 31 percent. A summary of accumulation mode aerosol integral size parameters is given in Table 14.

TABLE 14. PLUME ACCUMULATION MODE INTEGRAL SIZE PARAMETERS

Downwind Distance (km)	Accumulation Mode Volume, V_a ($\mu m^3/cm^3$)	Accumulation Mode Mean Size, D_a (μm)	
	San Manuel Smelter (10/4/77)		
60	9.9	0.18	2.0
127	12.9	0.14	1.9
Background	3.5	0.24	2.2
	Mohave Power Plant (10/8/77)		
32	5.0	0.23	2.1
62	4.7	0.19	2.1
Background	2.8	0.20	2.1

Sulfur Transformation

The conversion of SO_2 to particulate sulfate in plumes can be estimated from the measurements of gaseous SO_2, particulate sulfate, light scattering coefficient, and mean accumulation mode volume. A number of methods to determine SO_2 conversion rates in power plant plumes have

been used in the past (Wilson, 1978). The approach used here compares the fraction of particulate sulfur of the total sulfur, S_p/S_T, to plume age, estimated from analysis of winds aloft. Plume excess sulfur values with background subtracted were used in this calculation. The SO_2 conversion rate measured in the San Manuel smelter plume on October 4, 1977, from 0900 to 1230 MST was measured to be 0.7±0.2 percent/hour between 60 127 km downwind from the plant (Figure 14). This calculation assumes no SO_2 deposition between measurements. However, even as much as 20 percent SO_2 deposition would not lower the conversion rate below the stated uncertainty. The SO_2 conversion rate was not calculated for the Mohave power plant plume because of poor plume resolution and erratic wind behavior encountered on October 8, 1977.

This single measurement of the $SO_2 \rightarrow SO_4^=$ conversion rate should not be considered typical without many additional measurements under a variety of conditions. It is interesting to note, however, that this value is within the range of conversion rates measured in plants in the midwest (Husar et al., 1978).

A number of other parameters can be used as qualitative indicators of SO_2 conversion, such as plume excess b_{sp}/S_g, S_p/S_g, and mean accumulation mode volume $(V_a)/S_g$ ratios and accumulation mode aerosol size, D_{V_a}. These indicators are shown graphically in Figure 15 as a function of distance downwind from the plant for the San Manuel smelter and Mohave power plant plumes on October 4, 1977, and October 8, 1977, respectively. The three plume excess parameter ratios all increase downwind in both plumes, indicating that sulfur aerosol is being formed. The mean accumulation mode size decreases downwind from both plants which also indicates fresh aerosol is being formed.

One method of assessing the effect of sulfur transformation on visibility is to determine the improvement of visual range if no SO_2 was converted to sulfate. This can be estimated for the San Manuel smelter at 20 and 32 km downwind on October 2, 1977, assuming that the b_{sp}/SO_2 ratio remains constant beyond 8 km downwind. The visual range with the plume present is then calculated using b_{scat} and assuming no conversion, as described previously. This approach will slightly overestimate the effect of aerosol dilution (and therefore visual range) due to loss of SO_2 from the plume because of deposition and transformation. The results of this calculation are shown in Figure 16. At 32 km downwind from the smelter on October 2 the visual range would increase by nearly a factor of two if no SO_2 were converted to sulfate. At 60 km downwind the visual range would be increased by 36 percent if there were no conversion. Thus sulfur transformation has a large effect on visibility impairment within at least 60 km of the shelter.

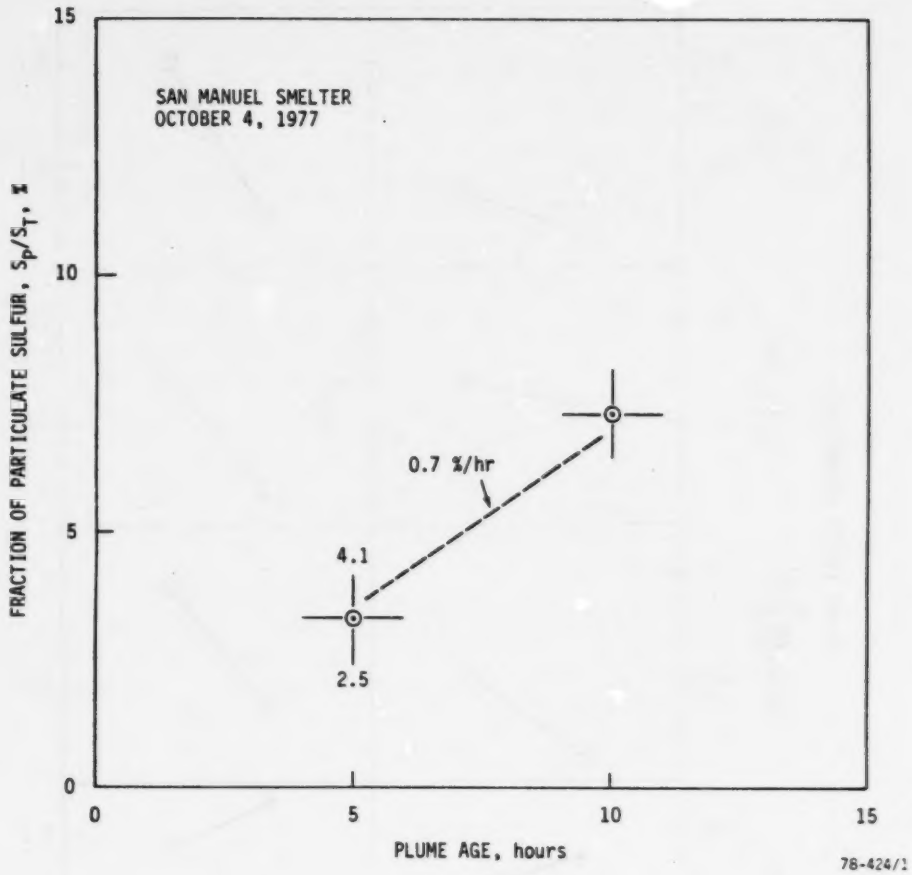


Figure 14. Determination of SO_2 conversion rate for the San Manuel smelter on October 4, 1977, from the fraction of particulate sulfur vs. plume age.

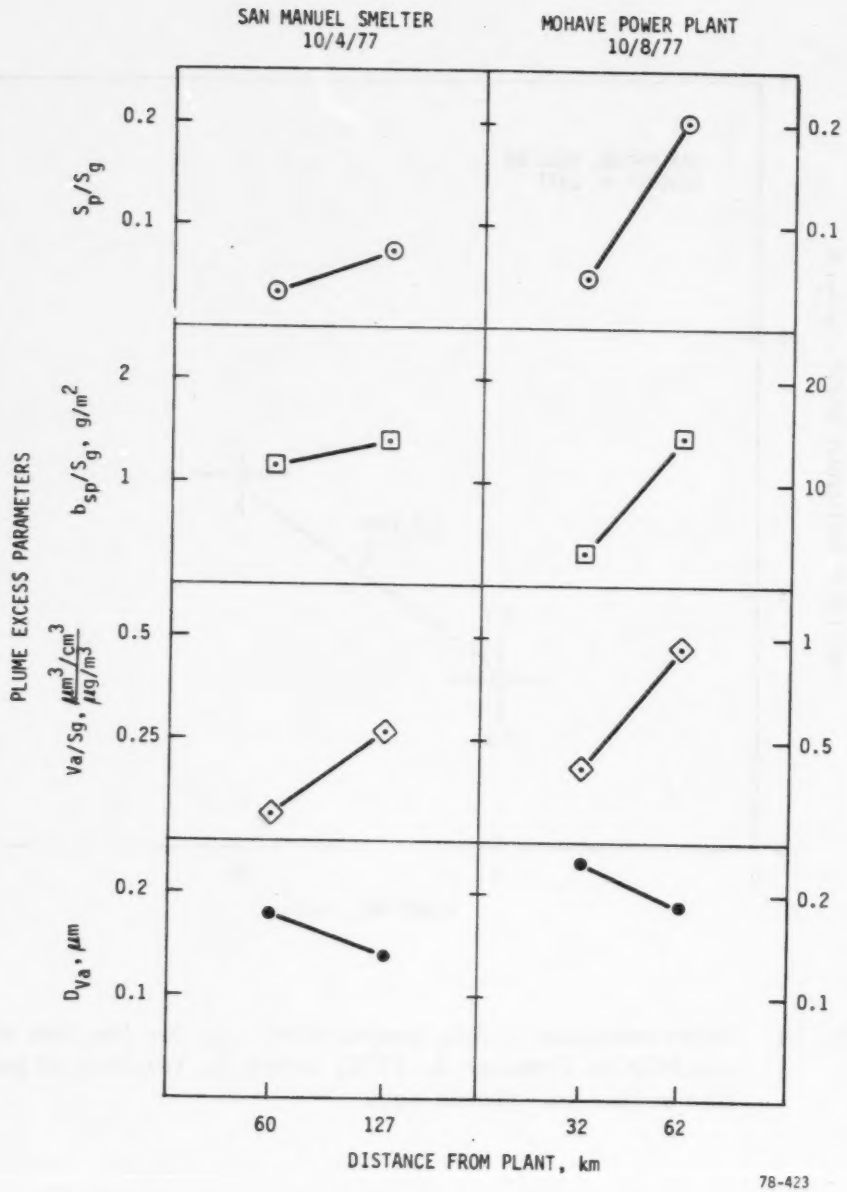


Figure 15. Qualitative indicators of SO_2 conversion in plumes plotted vs. distance from plant.

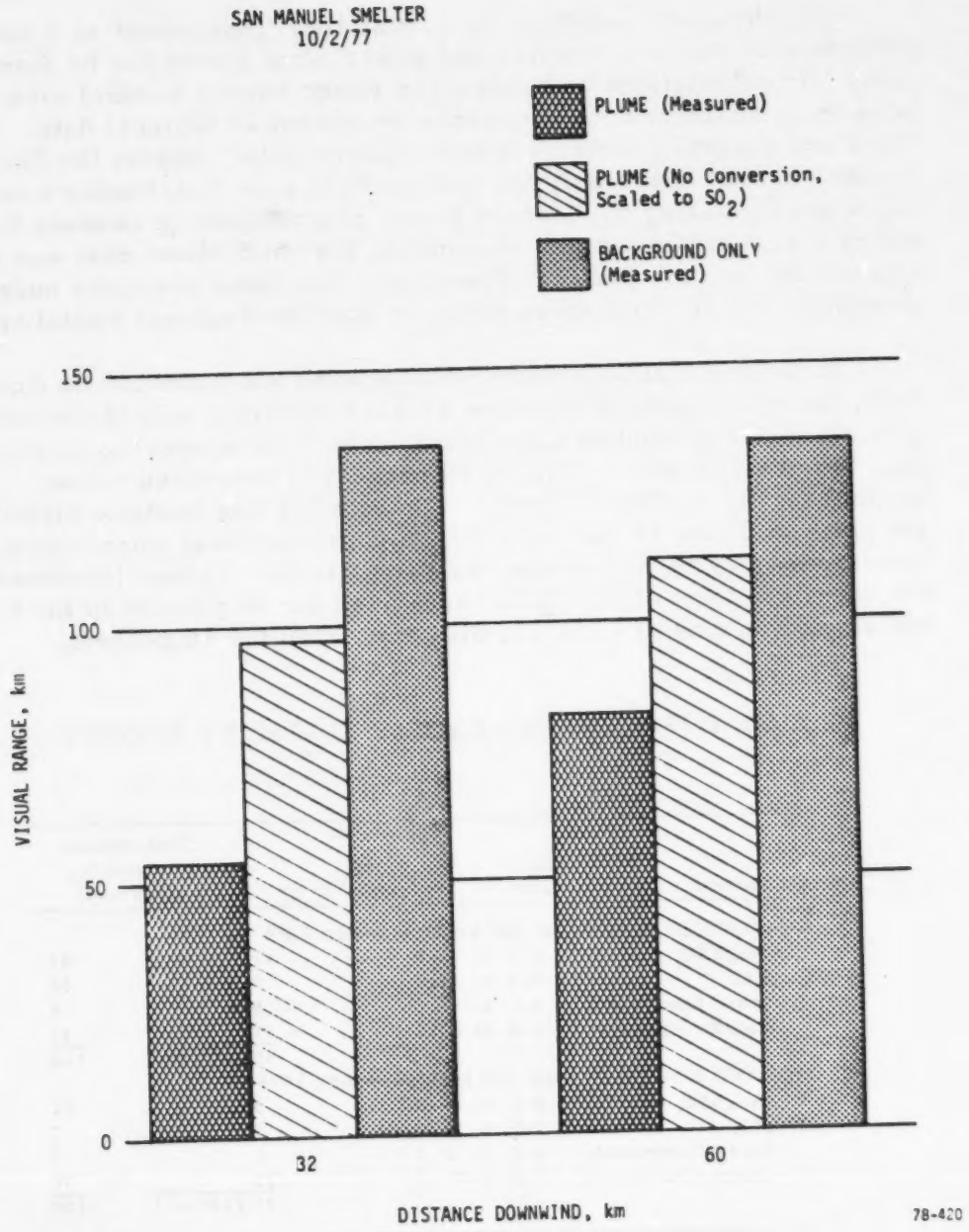


Figure 16. Visual range through San Manuel smelter plume with and without SO_2 conversion and through background only for two downwind distances.

Light Scattering Budget in Plumes

The detailed contributions to visibility impairment as a function of particle size due to a smelter and power plant plume can be determined using Mie calculations and measured plume excess aerosol size distributions in an analogous manner to the treatment of regional data. However, there are several problems with the plume data. During the San Manuel smelter plume flights only the fine particle size distribution was measured ($D_p \leq 1\,\mu m$). During the Mohave power plant flights on October 8, 1977, the entire size distribution was measured, but wind-blown dust was occasionally mixing into the plume. Therefore, the plume visibility budgets must be considered as much more tentative than the regional visibility budget.

In the San Manuel smelter plume at 62 km downwind on October 4, 1977, the plume excess b_{sp} value synthesized from only the measured fine particle size distribution ($D_p \leq 1\mu m$), using Mie scattering functions, was $\Sigma b_{sp} = 56 \times 10^{-6} m^{-1}$. This is 59 percent of measured value: b_{sp}(measured) $= 95 \times 10^{-6} m^{-1}$. The detailed fine particle visibility budget given in Table 15 was determined from chemical composition and size distribution, using Mie scattering calculations. Sulfate [assumed to be in the chemical form of $(NH_4)_2SO_4$] accounted for 43 percent of the total b_{sp} in the smelter plume of 10/4/77; SiC_2 accounted for 10 percent.

TABLE 15. PLUME EXCESS VISIBILITY BUDGET

Component	D_p (μm)	b_{sp} ($\times 10^{-6} m^{-1}$)	Contribution to total b_{sp} (percent)
SAN MANUEL SMELTER (62 km downwind) 10/4/77			
$(NH_4)_2SO_4$	0.1 to 1.0	41	43
SiO_2	0.1 to 1.0	9.5	10
Other Compounds	0.1 to 1.0	5.5	6
Coarse Particles	1.0 to 20.0	39	41
		$95 \times 10^{-6} m^{-1}$	100
MOHAVE POWER PLANT (32 km downwind) 10/8/77			
$(NH_4)_2SO_4$	0.1 to 1.0	3	11
SiO_2	0.1 to 1.0	2	7
Other Compounds	0.1 to 1.0	1	4
Coarse Particles[c]	1.0 to 20.0	21	78
		$27 \times 10^{-6} m^{-1}$	100

[a] Assumes that all fine particle sulfate exists as ammonium sulfate.

[b] Assumes that all fine particle silicon exists as SiO_2.

[c] Determined from b_{scat}(total) - b_{scat}(fine particles).

The Mohave power plant plume excess b_{sp} calculation on October 8, 1977, at 32 km downwind was $\Sigma b_{sp}(calc) = 27 \times 10^{-6} m^{-1}$, while the measured value was $18 \times 10^{-6} m^{-1}$. This difference may be due to the loss of large particles in the nephelometer sampling line.

Calculations of the light scattering budget for the Mohave power plant are complicated by the fact that aerosol composition calculations account for only about fifty percent of the fine particle aerosol mass as estimated from aerosol volume measurements. Therefore, the estimated contributions of individual chemical special to b_{sp} may be somewhat high. The visibility budget for the Mohave power plant plume at 32 km downwind on October 8, 1977, is quite different from the smelter results. Coarse particles account for 78 percent of the calculated b_{sp}. This high value is at least partially due to wind-blown dust mixing into the power plant plume at the time of the measurement. Fine particle ammonium sulfate accounted for 11 percent of b_{sp} ($b_{sp}[(NH_4)_2SO_4] = 3 \times 10^{-6} m^{-1}$). Fine particle silicon accounted for 7 percent of b_{sp} in the Mohave plant.

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